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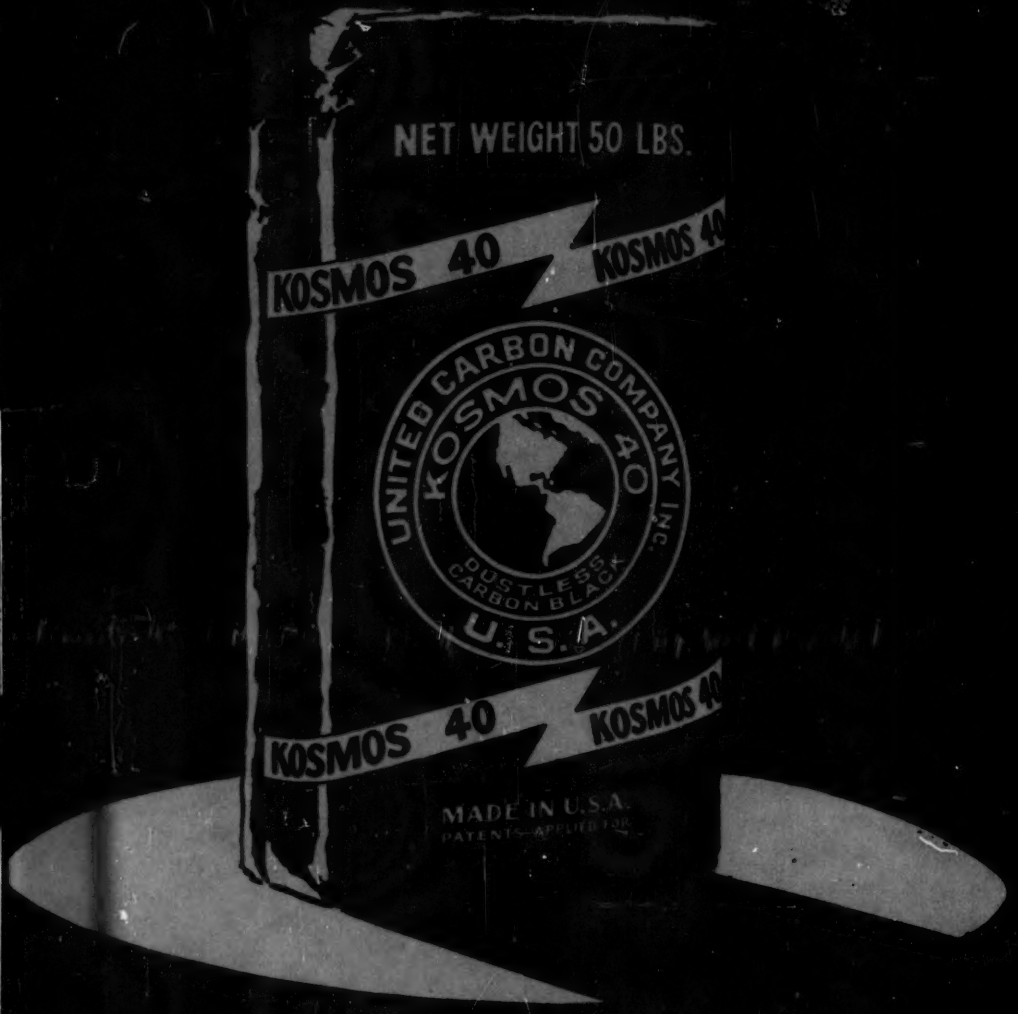

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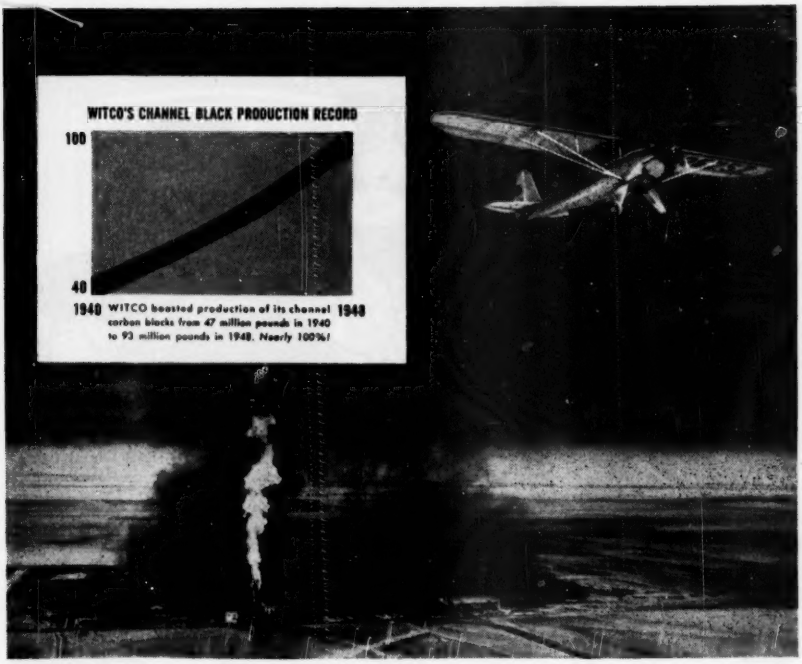
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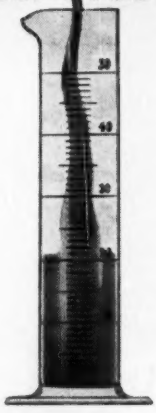

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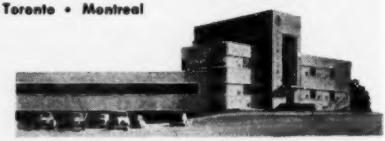

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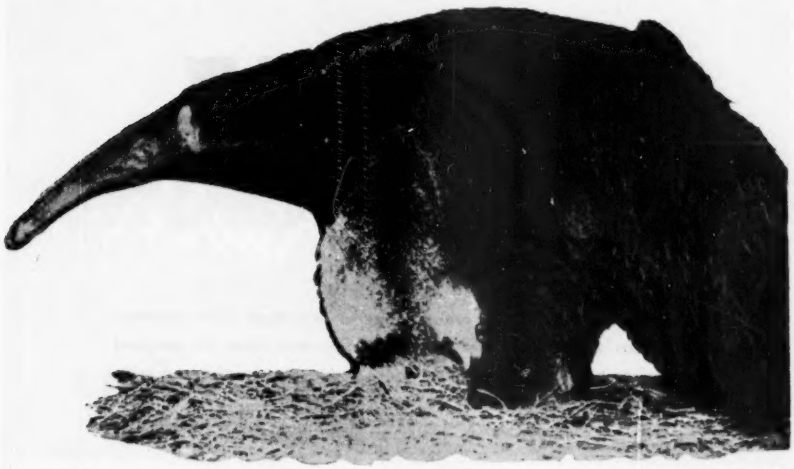

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Vol. XXIII **January-March, 1950** **No. 1**

CONTENTS

General Section PAGE

Officers iii
To All Readers of Rubber Chemistry and Technology v
The Institution of the Rubber Industry London vi
Fall Meeting of the Division of Rubber Chemistry vii
New Books and Other Publications viii

Reprinted Papers

Investigations in the Field of Rubber Vulcanization. IV. Phenomenon of Vulcanization Optimum in Mixtures with A Large Proportion of Constructive Agent. B. DOGADKIN AND B. KARMIN 1
Dependence of Elastic Properties of Vulcanized Rubber on the Degree of Cross-Linking. PAUL J. FLORY, NORMAN RABJOHN, AND MARCIA C. SHAFFER 9
Dependence of Tensile Strength of Vulcanized Rubber on the Degree of Cross-Linking. PAUL J. FLORY, NORMAN RABJOHN, AND MARCIA C. SHAFFER 27
Relationship Between Gough-Joule Coefficients and Moduli of Vulcanized Rubbers. F. S. CONANT, G. L. HALL, AND G. R. THURMAN 44
Time and Stress Effects in the Behavior of Rubber at Low Temperature. J. R. BEATTY AND J. M. DAVIES 54
Flow Phenomena in Rubber Samples. FRITZ RÖSSLER 67
Determination of the Molecular Weight of Rubber and Polystyrene by the Methods of Light Scattering and Osmometry. B. DOGADKIN, I. SOBOLEVA, AND M. ARKHANGEL'SKAYA 89
Infrared Studies of 1,2- and Trans 1,4-Structure of Polybutadiene and Butadiene-Styrene Copolymers Polymerized at Various Temperatures. E. J. HART AND A. W. MEYER 98
Some Problems Involved in the Grading and Testing of Natural Rubber. A Progress Report. W. P. FLETCHER 107
Effect of Soil Microörganisms on Rubber Insulation. JOHN T. BLAKE AND DONALD W. KITCHIN 117

Tear Initiation and Tear Propagation. J. M. Buist 137
The Velocity of Propagation of Ultrasonic Waves and the Form of the Molecules of High Polymers. Giulio Natta and Mario Baccaredda 151
Propagation of Audiofrequency Sound in High Polymers. R. S. Witte, B. A. Mrowca, and E. Guth 163
Propagation of Ultrasonic Bulk Waves in High Polymers. Donald G. Ivey, B. A. Mrowca, and Eugene Guth 172
Mastication of Rubber. I. A. van Rossem and J. Hoekstra 185
Mastication of Rubber. II. J. Hoekstra and A. van Rossem 196
Effect of Chemical Agents on Heat Deterioration of GR-S. Robert B. Mesrobian and Arthur V. Tobolsky 205
Plasticizers for Polar Synthetic Rubbers. La Verne E. Cheyney 217
Role of Adsorption in Reinforcement of GR-S. C. E. Barnett and H. C. Jones 229
Improved-Processing GR-S by Variations in Compounding. R. A. Crawford and G. J. Tiger 242
Characteristics of Reinforcing Furnace Blacks. Processing Shrinkage. E. M. Dannenberg and C. A. Stokes 252
The Compounding of Hard Rubber (Natural and Synthetic). W. Murray Gall 266
Bonding of Rubber to Metal by Means of New Chemical Derivatives of Rubber. Jacques Gossot 281
Color Reactions of Some Accelerators in Current Use. W. Schaefer 292
The Estimation of Small Percentages of Rubber in Fibrous Materials. C. M. Blow 300

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TO ALL READERS OF RUBBER CHEMISTRY AND TECHNOLOGY

The Division of Rubber Chemistry and the Institution of the Rubber Industry have come to a mutual understanding that membership in both organizations, exchange of papers, and coöperative effort in general are much to be desired, and that members of the rubber industry both here and overseas will derive great benefit from this coöperation.

As a beginning of this worthy effort, RUBBER CHEMISTRY AND TECHNOLOGY is glad to publish the following invitation of the Institution to members of the Division of Rubber Chemistry and to others interested in the promotion of all that the Institution symbolizes and actively fosters.

On the part of the Institution also, a cordial invitation is extended to young Americans and Canadians to attend courses with Europeans, South Africans, Australians, Indians, and others at the newly founded National College of Rubber Technology in London.

The Institution would like to receive papers in increasing numbers from rubber scientists and technologists for publication in the Transactions; to arrange lecture tours in different countries; to send delegates to rubber conferences; to present papers at these conferences; and to have all countries represented at the summer vacation residential courses which the Institution proposes to hold at one of the colleges at Oxford.

The achievement of these great and worthy aims by the Institution will benefit the entire rubber industry, and the support of rubber manufacturers, scientists, technologists, and executives in the United States and Canada is needed to carry out the program in the Western Hemisphere.

The Institution of the Rubber Industry London

The rubber industry owes its development largely to scientific and technical research, and the Institution was founded in 1921 to foster scientific and technical advancement and to disseminate the results.

THE INSTITUTION today is the centre of a great fraternity of rubber manufacturers, scientists, technologists, research establishments, executives, and students from every country, whose object is the advancement of the cause of the rubber industry throughout the world.

OBJECTS

To promote corporate and concerted effort in the industry by bringing together all those engaged or interested in the various branches of science and technology on which the Industry is based and coördinating their respective contributions.

To promote the profession and practice of rubber technology.

To encourage the extension of scientific and technical education in the principles and details of rubber manufacture.

To maintain a scheme of diplomas for the recognition of efficiency in knowledge of all branches of technology essential to the successful maintenance and development of rubber manufacture.

To arrange for the holding of meetings, the reading of papers, and the giving of lectures, with subsequent discussions and publications.

To foster the systematic study of scientific and technical problems involved in the various phases of the manufacture of natural and synthetic rubbers and rubberlike materials and their conversion into finished products.

To encourage original work and research dealing with the manufacture of rubbers.

PUBLICATIONS

The *Transactions*. A bimonthly record of scientific and technological investigations in the realm of rubber and its allied industries.

Annual Report on the Progress of Rubber Technology. This contains systematic accounts of the developments in rubber technology from year to year.

Proceedings of Rubber Technology Conferences.

INVITATION TO MEMBERSHIP

At this time of progress and expansion in the affairs of the Institution, its Council, conscious of the benefits that lie within the sphere of the Institution, invites applications for the privilege of membership from those engaged or interested in the rubber and allied industries.

Application forms and full particulars may be obtained from:

THE REGISTRAR
INSTITUTION OF THE RUBBER INDUSTRY
12, WHITEHALL
LONDON S.W. 1, ENGLAND

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY

September 21–23, 1949

Atlantic City, New Jersey

The 55th Meeting of the Division of Rubber Chemistry was held in conjunction with the 116th Meeting of the American Chemical Society. The Division headquarters was the Chalfonte-Haddon Hall Hotel, and the technical sessions, banquet, and committee meetings were all held in Haddon Hall.

Local arrangements were in the hands of a committee headed by L. K. Youse, assisted by F. M. Galloway, R. A. Kurtz, and W. B. Munroe. There were about 600 chemists and guests registered for the meeting, and approximately 450 attended the banquet.

The 25-Year Club luncheon was held under the Chairmanship of John P. Coe, with nearly 100 members present.

Nineteen papers were presented at three sessions—Wednesday afternoon, Thursday afternoon, and Friday morning. There were invited papers by G. S. Whitby, A. A. Morton, and J. R. Johnson.

At the Business Meeting, H. I Cramer announced the election of the following new officers and directors:

Chairman, F. W. Stavely; *Vice-Chairman*, J. H. Fielding; *Secretary*, C. R. Haynes; *Treasurer*, C. W. Christensen. *Directors: Director-at-Large*, S. G. Byam; *Akron*, A. E. Juve; *Boston*, F. H. Amon; *Buffalo*, A. H. Davis; *Chicago*, P. F. Niessen; *Connecticut*, C. M. Doede; *Detroit*, G. F. Lindner; *Los Angeles*, R. E. Hutchinson; *New York*, D. E. Jones; *Northern California*, A. E. Barrett; *Philadelphia*, L. K. Youse; *Rhode Island*, F. H. Springer; *Southern Ohio*, J. E. Feldman.

Due notice was taken of the recent loss by death of three of our members: Chester E. Linscott, A. Donald Cummings, and Laurence D. Ackerman.

E. H. Krismann reported for the Auditing Committee that they had made an audit of the books and found same to be in order.

Arthur E. Drake reported for the Membership Committee that, as of September 1, there were 2098 regular members and 323 associate—a total of 2421. He cited particularly the efforts of D. F. Behney of the Goodyear Tire & Rubber Co. and P. M. Nichols of the U. S. Rubber Co.

Chairman Cramer gave a short announcement of the Executive Committee activities, stating particularly the acceptances of the petition of the Washington Group to become a sponsored rubber group, and the election of C. C. Davis as Charles Goodyear Medalist. The Directors of the Washington Rubber Group are T. A. Werkenthin, President; R. J. Devereaus, Vice-President; and Norman Bekkedahl, Secretary-Treasurer. Chairman Cramer furthermore told the Division that the By-Laws were in process of revision, and that the members would receive a copy of the new By-Laws in time to vote on them at the next regular meeting.

The meetings in 1950 are to be with the American Chemical Society on April 19–21 at the Book-Cadillac Hotel, Detroit, and at Cleveland, October 11–13.

The following papers were presented:

1) Introductory remarks. H. I. CRAMER.
2) Some Problems Involved in the Grading and Testing of Natural Rubber. A Progress Report. W. P. FLETCHER.
3) Determination of the Refractive Index and Second-Order Transition Temperatures of Elastomers at Temperatures from 25° to −120° C. G. M. BRAUER AND R. H. WILEY.
4) Application of Microradiography to Rubber Compounding Problems. M. J. BROCK.
5) The Ultra-Speed Tensile of Rubber and Synthetic Elastomers. D. S. VILLARS.
6) Effects of Sulfur and Accelerator Variations on the Physical Properties of a "Cold Rubber" Tread Stock. L. R. SPERBERG.
7) Improvement of Dispersion of Benzothiazyl Disulfide in GR-S and Natural Rubber by Use of Fusion Mixtures with Sulfur. M. C. THRODAHL.
8) Mooney Scorch by Varying Temperatures. A. A. SOMERVILLE AND G. C. MAASSEN.
9) The Importance of Controlling Heat Losses in Molding Operations. R. E. SHRADER AND W. N. KEEN.
10) Polyamine-Activated Polymerization. G. S. WHITBY AND N. WELLMAN.
11) Alfin Catalysts for Polymerizing Butadiene. A. A. MORTON.
12) The Biosynthesis of Isoprenoid Structure. J. R. JOHNSON AND KOERT GERZON.
13) New Developments in Silastic. A. D. CHIPMAN, H. F. SCHMIDT AND G. M. KONKLE.
14) Properties and Utilization of Polyacrylic Rubbers. H. P. OWEN.
15) The Vulcanization of Neoprene Type W. D. B. FORMAN, L. R. MAYO AND R. R. RADCLIFF.
16) Stopping Agents for "Cold Rubber". L. B. WAKEFIELD AND R. L. BEBB.
17) Effect of Oxygen on Rate of Polymerization of GR-S in Various Low-Temperature Emulsion Systems. R. W. HOBSON AND J. D. D'IANNI.
18) Low Temperature Stiffening of Elastomers. S. D. GEHMAN, P. F. JONES, C. S. WILKINSON, JR. AND D. E. WOODFORD.
19) The Effect of Compounding Ingredients on the Weather Resistance of Neoprene Vulcanizates. D. C. THOMPSON AND N. L. CATTON.
20) Mechanism of Reënforcement. IV. Adsorption of GR-S by Carbon Black. LEONARD E. AMBORSKI, CARL E. BLACK AND GEORGE GOLDFINGER.

C. R. HAYNES
Secretary

NEW BOOKS AND OTHER PUBLICATIONS

PROCEEDINGS OF THE SECOND RUBBER TECHNOLOGY CONFERENCE, LONDON, JUNE 23–25, 1948. Edited by T. R. Dawson, with the assistance of C. M. Blow and G. Gee. Cambridge: W. Heffer and Sons, Ltd., on behalf of the Institution of the Rubber Industry, pp. xxxii+524+xx. 63s. 0d. net; 64s. 0d. post free.—In accordance with tradition, the *Proceedings of the Rubber Tech-*

nology Conference, held in London in June, 1948, have now been published in book form. The volume has been edited by T. R. Dawson (head of Intelligence Division, R.A.B.R.M.) with the assistance of C. M. Blow and G. Gee (B.R.P.R.A.). The chief feature of the book is represented by the "papers", of which there are 44, subdivided under the headings: Synthetic Rubbers; Chemistry of Rubber; Physics of Rubber; Testing and Analysis; Latices; Compounding Ingredients-General; Compounding Ingredients-Carbon Black; and Factory Processes and Products. Next in order of importance are the Discussions on the papers. There are those who regard international conferences on matters of industrial importance as little more than scientific or technological beanfeasts, but it does not need a profound study of the volume under review to appreciate that we have here a mirror of some of the latest developments in scientific and technical thought and the practical outcome of hard and unbiased work based on the knowledge and experience of the representatives of some 15 countries. The papers on technological and factory problems, as F. M. Panzetta (Chairman, Executive Committee) indicates in his Foreword, are not so numerous as those connected with the other subjects mentioned, but this shortage, as he says, must be put down to the brief time which has elapsed since the termination of the war. "The war", to quote Mr. Panzetta, further "acted as a stimulant to research and development in the rubber industry such as it has never had before but, equally the need for secrecy suppressed from published technical literature much of the results of this work". The need for much of this secrecy has now disappeared, and so far as was practicable or desirable those reading papers, or taking part in the discussions, seem to have been conscious of their new liberty in this connection. Hence the contents of the Conference book are of more than ordinary interest, if we measure interest by the yardstick of pre-war conferences. However, quite apart from matters bearing on war work, the scientific and technological matter in the volume place it above the average of publications of a similar type. [From the *India Rubber Journal*.]

THE PHYSICS OF RUBBER ELASTICITY. L. R. G. Treloar. London: Oxford University Press, 1949, pp. viii+256. 21s. 0d. net; 21s. 7d. post free.—Many in recent years have queried the value of fundamental work on the structure and properties of rubber, but, in truth, this view is a sad indication of a misunderstanding which is too common in many industries to-day. No sustained progress can be made in technology without a knowledge of the underlying principles involved. As Dr. Treloar points out in the preface to his book, ". . . in any type of work involving experimentation it is impossible to get along without some sort of theory, however limited or *ad hoc* it may be . . . if one is going to have a theory at all one may as well take some trouble to find the one which most nearly represents the known facts". It is the background of fundamental theory which provides the practical technologist with the inspiration for his inventive genius. And how seldom is the fundamental research worker given credit for this indirect but nevertheless essential contribution to technological advance? Dr. Treloar's book describes with unusual clarity the development of the modern statistical theory of rubber elasticity. The statistical or kinetic theory is developed from the early work of Meyer, von Susich and Valko, through that of Flory, Kuhn, and Guth, and is shown to give a good explanation of the mechanical and photoelastic properties of rubber. The book also discusses crystallization, stress relaxation, the dynamic

properties of rubber, and the solution of problems involving large elastic strains. Most of these subjects have been dealt with in several books recently published, but the whole theory of rubber elasticity has never before been discussed so simply and yet so authoritatively as in the present work. Dr. Treloar's command of his subject, coupled with a delight in plain English, makes his book a pleasure to read, and there is no doubt that it will be for many years an inspiration to all who strive with rubber. The rubber technologist is presented with a comprehensive working theory in concise form on which he can soundly develop his approach to his more practical everyday problems. The book is splendidly printed and the text seems to be almost completely free of misprints and similar errors. [From the *India Rubber Journal.*]

RUBBER RED BOOK. 1949 Edition, Seventh Issue. Published by *The Rubber Age*, 250 W. 57th St., New York 19, N. Y. Cloth, 6 by 9 inches, 924 pages. Price $5.—Continuing the expansion in size of the previous editions, this issue of the "Red Book" shows a total increase in number of pages, including advertisements, of 88 over the sixth issue. This increase in total pages is reflected by corresponding increases in the different sections of the book, particularly in the number of rubber manufacturers. The organization and classification system remains the same, except for the inclusion of a new section on educational courses in rubber chemistry and technology. The directory includes sections on rubber manufacturers in the United States and Canada, rubber machinery and equipment, accessories and fittings, rubber chemicals and compounding ingredients, fabrics and textiles, natural rubber and related materials, synthetic rubbers and other rubberlike materials, reclaimed rubber, scrap rubber dealers, rubber latex, rubber derivatives, miscellaneous products and services, consulting technologists, branch offices and sales agents, trade and technical organizations, the new section on educational courses, technical journals, and a who's who in the rubber industry. Both subject and advertisers indices are appended. [From the *India Rubber World.*]

FRENCH-ENGLISH VOCABULARY. Technical Terms Used in Connection with Rubber. Report R-56. February 1949. Unbound, 6×9 inches. 19 pages.

GERMAN-ENGLISH VOCABULARY. Technical Terms Used in Connection with Rubber. Report R-57. May 1949. Unbound, 6×9 inches. 40 pages. Imperial Chemical Industries, Ltd., London, S.W. 1. Both gratis.—The French-English vocabulary is a new publication; the German-English one is a revision and enlargement of an earlier issue (Report R-49). Both were prompted by the favorable reception accorded the German-English Vocabulary. They are welcome contributions by the ICI, and should be valuable to a great number of rubber chemists and technologists, who, as one of our eminent rubber scientists recently remarked, must again read the European literature, whether they want to or not. The French vocabulary is restricted to nouns; the German to nouns and a few adjectives. This is, of course, unfortunate, but it may be the only way to prevent the vocabularies from growing to small dictionaries. However, it does appear inconsistent to omit all verbs, yet consume space with words such as absorption, adhésion, adsorption, coagulation, déformation, dispersion, fatigue, gel, hystérésis, joint, microscope, relaxation, rupture, and others which are exactly the same in French and English, or even with words such as carcasse, conductivité, copolymère,

crêpe, diaphragme, élasticité, floculation, hypothèse, masse, paraffine, plasticité, polymère, porosité, viscosité, etc., which are obvious. This applies to a much less degree to the German vocabulary, because scientific and technical words similar to the corresponding ones in English are far less numerous in German. It would seem better to omit all words the meanings of which are evident, and add at least a few verbs or adjectives, the meanings of which in the rubber industry differ from their ordinary meanings. For lack of verbs in the vocabularies, let us choose a random noun as a very good example. The ordinary dictionary defines *boudinage* as the roving or twisting of textile fibers, whereas the ICI vocabulary defines it for the rubber technologist as *extrusion*. If some well chosen verbs and adjectives with specialized meanings were to be included in a corresponding manner, the ICI vocabularies would be still more valuable. Nevertheless the fact that they contain so many nouns, the meanings of which are not given by ordinary dictionaries, makes the vocabularies almost indispensable to the busy rubber scientist and technologist. The ICI is, therefore, to be congratulated and thanked for its valuable contribution to the rubber industry, which is confronted more and more with important literature in the French and German languages.

THE THEORY OF SOLUTIONS OF HIGH POLYMERS. A. R. Miller, Oxford University Press, 114 Fifth Ave., New York 11, N. Y. Cloth, 5½ by 8½ inches, 124 pages. Price, $3.25.—This monograph is an exposition of the mathematical advances in the treatment of solutions of high polymers which have been made during the last decade. The first chapter describes the model of a liquid which is used and reviews the nature of a partition function and its use in the theory of solutions. The application of the model to solutions of high polymers and the difficulties which arise in the evaluation of their statistical and thermodynamical functions are examined in the second chapter. The next two chapters develop the theory and examine its application to available experimental data. Chapter V examines the effect of the energy of mixing; while the concluding chapter discusses various reasons for existing discrepancies between theory and experiment and suggests lines for further research. The approach to the subject is mathematical throughout and, while of little interest to those unacquainted with statistical methods and thermodynamics, will be of value to advanced workers in the field. [From the *India Rubber World*.]

MONOMERS, Section I: A Collection of Data and Procedures on the Basic Materials for the Synthesis of Fibers, Plastics, and Rubbers. Edited by E. R. Blout, H. Mark, and W. P. Hohenstein. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. Cloth, looseleaf, 6½ by 9½ inches, 343 pages. Price, $7.50.—This compilation brings together in one place much of the data on properties, production processes, reactions, etc., of monomers previously appearing in widely scattered form throughout the literature. This section comprises eight pamphlets covering production, purification, analysis, handling, physical and chemical properties, reactions, and polymerization of acrylonitrile, butadiene, isobutylene, isoprene, styrene, methyl methacrylate, vinyl acetate, and vinyl chloride. Chapters on acrylate and methacrylate esters, and acrylic acid are in preparation; material on other monomers and additions to the present collection will be published as necessary. Although production methods are discussed in detail, in several cases current methods are not described. Other failings include the use of relatively few late refer-

ences, and rather brief discussions of chemical reactions and polymerization methods. The sections on physical properties are comprehensive, however, and the book will be of value as a source of data on properties and behavior of monomers. [From the *India Rubber World.*]

MODERN PLASTICS ENCYCLOPEDIA. (1949 EDITION). Modern Plastics, Inc., 122 East 42nd St., New York 17, N. Y. 9×12 in. 1370 pp. $5.00.—Designed as a comprehensive working guide to all phases of plastics planning and production for companies using or contemplating the use of plastics products or components, this encyclopedia presents also a complete picture of the technical advances made in the plastics industry during the past 12 months. Characteristic of the encyclopedic scope of the work are the numerous charts and tables containing complete chemical formulas, physical and chemical properties and ASTM specifications. A striking feature of the new work is a "Plastics in Use" section which analyzes more than 1,000 successful applications of plastics in 27 basic industrial fields ranging from building materials to toys and novelties. Other sections of the book provide detailed information on types of plastics materials, designing in plastics, selection of raw materials and manufacturing techniques. The needs of plant superintendents and plant engineers are met in chapters on molding, extruding, casting, fabricating, finishing and assembling operations, and the machines and equipment presently available. A buyers' guide is also offered for the company purchasing agent. This valuable reference work is presented in a one-volume edition, unlike other recent editions, which were separated into one or more volumes. [From the *Rubber Age* of New York.]

PLASTICS IN ENGINEERING. John Delmonte. Penton Publishing Co., Penton Bldg., Cleveland 13, O. Cloth, 6 by 9 inches, 654 pages. Price, $10.—This third edition of what has become a standard textbook on plastics engineering has been extensively revised, and a great deal of new information included on recent developments. The chapters follow a pattern of materials, properties, methods, and applications, with emphasis on engineering data. The technical data are organized to permit easy reference, and the use of numerous diagrams, photographs, tables, and other figures adds greatly to the clarity of the text and the value of the book. Chapter headings include an introduction to organic plastics; types, characteristics, and preparation of organic plastics; effects of fillers on the properties of molded plastics; physical properties of plastic materials; thermal properties; electrical properties; chemical properties; optical properties of transparent plastics; design principles for molded plastic parts; inserts for molded plastics; characteristics and preparation of molding compounds; compression and transfer molding; injection molding; cold molding; design and construction of molds; laminated plastics; cast plastics; extrusion of plastics; nonmetallic bearings and their uses; nonmetallic gears and pinions; nonmetallic cams, couplings, and clutches; engineering applications of plastics; engineering applications of transparent plastics; styling the machine with plastics; plastics fabricating and finishing; organic plastics in surface coatings; synthetic rubbers and rubberlike materials; common failures and defects in plastics materials; and comparative costs of plastics and molds. The usefulness of the book is further enhanced by the inclusion of a comprehensive 16-page subject index. [From the *India Rubber World.*]

INVESTIGATIONS IN THE FIELD OF RUBBER VULCANIZATION. IV. PHENOMENON OF VULCANIZATION OPTIMUM IN MIXTURES WITH A LARGE PROPORTION OF CONSTRUCTIVE AGENT *

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In Part I of this investigation[1], the present authors developed the concept that the phenomenon of a vulcanization optimum, *i.e.*, the existence of a minimum or maximum on the kinetic curves describing the variation of a number of properties of mixtures subjected to vulcanization, is explained by the fact that vulcanization involves a superimposition of oppositely directed processes, some of which lead to a building-up of the structure of the rubber hydrocarbon, while others tend to result in its disintegration. On the basis of this concept, there was derived the following equation to describe the kinetics of strength variation during the vulcanization of mixtures prepared from natural rubber:

$$\pi = \pi_0[1 + a(1 - e^{-k_1\tau})][1 - b(1 - e^{-k_2\tau})],$$

where π is the tensile strength at the instant τ; π_0 is the tensile strength of the unvulcanized mixture; k_1 is the kinetic constant of the sulfur-addition process (constructive process); k_2 is the kinetic constant of the oxygen-addition process (destructive process); and a and b are constants which relate the change in strength to the respective quantities of sulfur and oxygen combined with the rubber. The applicability of this equation was demonstrated in the case of a large number of mixtures of various compositions and embodying different accelerators, as long as the sulfur content of these mixtures did not exceed 3 per cent of the rubber. In the case of mixtures containing 7 per cent and over, the equation was not valid, although the phenomenon of a vulcanization optimum still prevailed. In a number of cases, the vulcanization of mixtures prepared with sodium-butadiene and butadiene-styrene rubbers also failed to conform to the above equation.

Comparison of Figures 1 and 2 shows the difference in the vulcanization kinetics of natural rubber mixtures containing 2 and 7 per cent of sulfur, respectively. In mixtures with a low sulfur content, the maximum strength value ("strength optimum") occurs at the instant when nearly all of the sulfur has combined with the rubber. As already noted, sulfur plays the part of a constructive agent, and the increase in the strength of the mixture proceeds, as a first approximation, in linear correlation with the quantity of combined sulfur. The descending branch of the strength curve corresponds to the period when (following exhaustion of the sulfur) the continuing action of oxygen as a

* Translated for Rubber Chemistry and Technology by Alexander Bogrow, Cambridge, Mass., from the *Kolloidnii Zhurnal (Colloid Journal, U.S.S.R.)*, Vol. 9, No. 5, pages 348–354 (1947).

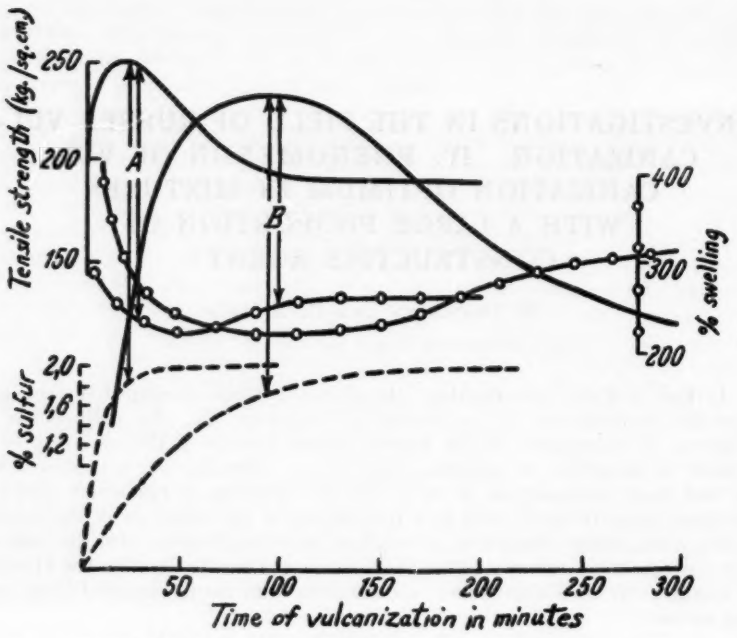

FIG. 1.—Vulcanization kinetics of natural-rubber mixtures containing 2 per cent sulfur. Arrows connect curves of each mixture. A—Mercaptobenzothiazole accelerator. B—Diphenylguanidine accelerators.

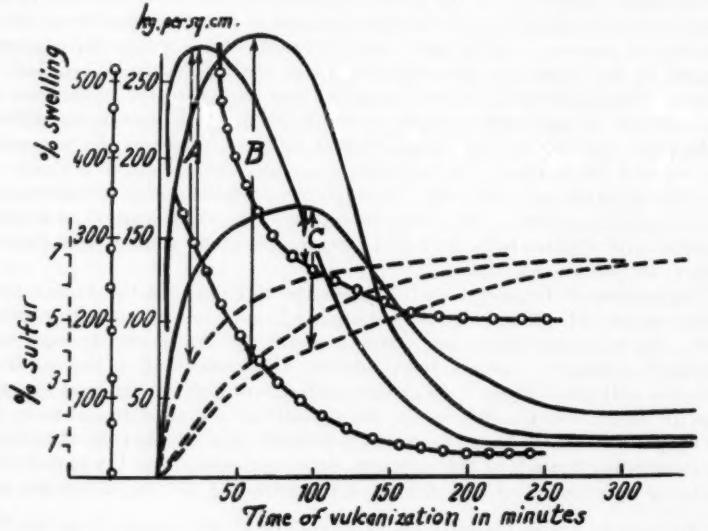

FIG. 2.—Vulcanization kinetics of natural-rubber mixtures containing 7 per cent sulfur. A—Mercaptobenzothiazole. B—Diphenylguanidine. C—No accelerator.

destructive agent is observed. For the same reason, the kinetic curve representing the swelling capacity of the vulcanized mixture in gasoline shows a minimum which coincides in time with the strength maximum. The unvulcanized mixture possesses unlimited swelling capacity in gasoline; as vulcanization progresses, the building-up of the structure of the mixture (the interlinking of molecular chains by sulfur atoms) leads to a reduction in the swelling capacity. At the instant when the constructive processes are most pronounced (at the vulcanization optimum), the mixture possesses its minimum swelling capacity; the subsequent recovery of this property is the result of a process of oxidative destruction of the rubber hydrocarbon.

During the vulcanization of mixtures with a higher sulfur content (7 per cent and higher), the maximum strength occurs before the sulfur is completely exhausted, *i.e.*, when the quantity of combined sulfur, regardless of the type of accelerator employed, constitutes about 3.5 per cent of the rubber. In this case, the swelling curve of the mixtures is monotonic in character, and approaches a limiting value without passing through a minimum. Such a character of the variation in the properties of the mixture does not make it possible to interpret the decrease in strength following the vulcanization optimum as a result of a destructive process brought about by the action of molecular oxygen. It is obvious that, during this period too, the building-up of the structure as a result of a continuing addition of sulfur predominates over the disintegration caused by the action of oxygen. In the contrary case, the swelling curve during this period would show an ascending branch, as observed in mixtures with a low sulfur content.

To explain the existence of a maximum on the kinetic strength curve during vulcanization of mixtures with a higher sulfur content, we propose the following hypothesis. It is known that the tensile strength of vulcanizates produced from different types of rubbers depends on the quantity of crystalline phase, or, in the general case, on the quantity of the highly oriented part of the rubber hydrocarbon formed as a result of tension prior to the point of rupture. For this reason, pure vulcanizates, which crystallize when the rubber is stretched, show a strength that is about one order of magnitude higher than the strength of vulcanizates produced from rubbers incapable of crystallization. In our laboratory, B. V. Lukin determined the crystalline-phase content of various vulcanizates after an elongation of 500 per cent by measuring the intensity of crystalline interferences in x-ray diffraction patterns with respect to the intensity of the amorphous halo.

As is seen from Figure 3, the strength of vulcanizates differing from one another in their sulfur content or type of accelerator is, as a first approximation, at the vulcanization optimum, a linear function of the quantity of crystalline phase. There can be no doubt that the capacity for crystallization under tension (or, in the more general case, the ability to form molecular chains that are perfectly oriented in the direction of elongation) depends on the character of the internal structure of the vulcanizates. The vulcanizing agent establishes a connection between the molecular chains of the rubber, forming bridges with the aid of main-valence forces (intermolecular constructive reactions), or else with the aid of molecular attraction forces. Therefore, as a result of vulcanization, a space lattice is produced from the molecular chains. This lattice becomes denser as the content of the constructive vulcanization agent increases; the strength of the lattice increases simultaneously. However, the strength of the vulcanizate lattice increases only until it becomes so dense that it begins interfering with the orientation of the chains. When the lattice

becomes sufficiently dense, the mobility of the molecular chains is restricted, their orientation is inhibited, and consequently the quantity of crystalline or highly oriented phase diminishes. In the case of sulfur-containing vulcanizates produced from natural rubber, this situation occurs as soon as about 3.5 per cent of sulfur combines with the rubber. After this point of vulcanization optimum is attained, a drop in the strength of the vulcanizate is observed.

Such an interpretation is also confirmed by the following very interesting fact. If the tensile strength of mixtures subjected to vulcanization is determined with a Schopper dynamometer at different rates of deformation, there is observed not only a change in the absolute values of the results, but also a shift of the optimum point with respect to the time of vulcanization.

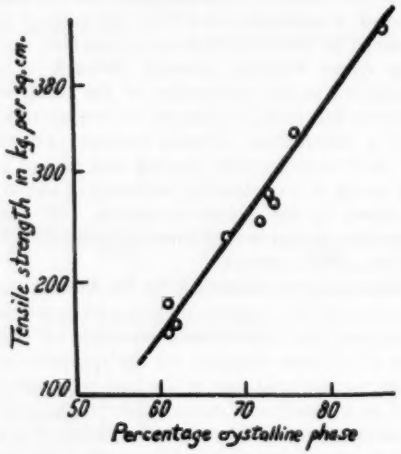

FIG. 3.—Tensile strengths of vulcanizates at the vulcanization optimum as a function of the proportion of crystalline phase formed during elongation to 500 per cent. Each point represents a vulcanizate characterized by its sulfur content or composition of accelerator group.

Figure 4 shows curves which demonstrate such a shift during the vulcanization of a mixture of the following composition (in parts by weight): smoked sheet 100, sulfur 7, zinc oxide 5, diphenylguanidine 0.38, stearic acid 2. The elongation rate was varied through the range of 50–500 mm. per minute. As is evident from Figure 4, the time required to attain the vulcanization optimum (maximum on the strength curve) increases appreciably as the rate of deformation is reduced. Such a phenomenon is not observed in mixtures with a low content of vulcanizing agent; it is explained by the fact that, as a result of the long relaxation time characteristic of the molecular chains of rubber, the higher the rate of deformation the fewer are the chains which are transformed into a perfectly oriented state. Thus, from the point of view of the formation of an oriented or crystalline phase, an increase in the rate of deformation acts in the same direction as the formation of a denser lattice. The higher the rate of deformation the less dense the lattice in the presence of which the strength curve shows a maximum. It is precisely this phenomenon which took place in our experiments.

In good agreement with the point of view outlined above is Field's observation[2] of the appearance of a maximum on a curve relating the percentage of crystalline phase to the time of vulcanization at a certain definite degree of elongation. This phenomenon was studied in greater detail in the work of Lukin and Kasatochkin[3], and will also form the subject of one of the subsequent communications from our laboratory.

The idea of the influence of the denseness of the space lattice of the vulcanizate on its strength, and in connection with this on the manifestation of the vulcanization-optimum effect, does not contradict our earlier considerations[4] relating to the existence during vulcanization of oppositely directed constructive and destructive processes, the combination of which leads to kinetic curves of a special type, possessed of a minimum or maximum. An increase in the denseness of the lattice may lead to the presence of a maximum on the curve showing variation of strength during the vulcanization process, but it cannot explain the appearance of a minimum on the solubility, swelling,

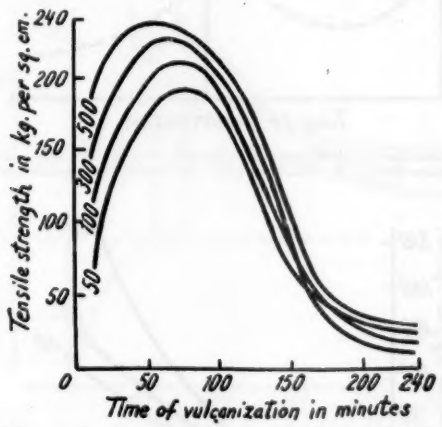

FIG. 4.—Kinetics of change in tensile strength during vulcanization. Numbers on the curves indicate the rate of deformation in mm. per minute.

or relative elongation curves. Thus, to permit solution of the question whether the vulcanization optimum is caused principally by the effects of oppositely directed processes or by the presence of a very dense lattice, the experimenter must have at his disposal not only data on the tensile strength of the material, but also parallel data on its swelling, relative elongation, and other characteristics.

Both cases of the vulcanization-optimum phenomenon are represented schematically in Figure 5. In the first case, in the presence of a combination of oppositely directed processes, the curves describing the variations in strength, swelling, and relative elongation have a maximum or a minimum. In practice, this case is realized whenever the effect of the destructive processes is commensurate with the effect of the constructive action of the vulcanization agent. It is precisely this which is observed during the vulcanization of natural rubber mixtures containing not over 3.5 per cent sulfur. Characteristic of such a case is the phenomenon of reversion of vulcanization, which is reflected in the

fact that the elongation isotherms of such mixtures beyond the vulcanization optimum lie lower than the analogous curves for the same mixtures at the vulcanization optimum (Figure 6). In other words, in passing beyond the vulcanization optimum, the mixtures appear to soften (lower modulus, greater deformation); this may be the result of destructive processes in the vulcanizate.

In the second case, in which the vulcanization-optimum phenomenon is connected with an increasingly dense space-lattice in the structure of the vulcanizate, only the strength curve shows the presence of a maximum. Since,

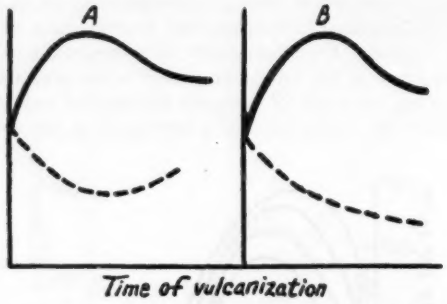

FIG. 5.—Schematic representation of kinetic vulcanization curves. A—Mixtures with low content of constructive agent. B—Mixtures with high content of constructive agent.

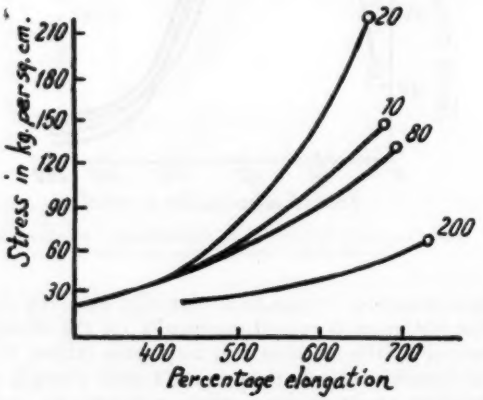

FIG. 6.—Elongation isotherms of a mixture of the composition: rubber 100, sulfur 2, mercaptobenzothiazole 0.6, zinc oxide 5, and stearic acid 2 parts. Numbers on the curves indicate the time of vulcanization in minutes.

in this case, the lattice continues becoming ever denser because of the absence of any destructive effect, the kinetic curves representing solubility, swelling, and relative and residual deformation descend monotonically.

In this case, the phenomenon of reversion of vulcanization is not observed. A case of this type is realized either if the content of constructive (vulcanizing) agent in the mixture considerably exceeds the content of destructive agent, or else if the destructive process is altogether absent. In particular, such a case

is observed during the vulcanization of natural rubber mixtures containing more than 7 per cent of sulfur. The vulcanization of certain synthetic rubbers is also extremely characteristic in this respect. As was previously established by one of us[5], molecular oxygen is a constructive agent for sodium-butadiene rubber under vulcanizing conditions, cross-linking the molecular chains to form a spatial structure; its action is similar to that of sulfur in secondary reactions. Thus, during the vulcanization of sodium-butadiene rubber, there is observed no opposition between the action of sulfur and oxygen. Both substances may be considered as constructive agents; moreover, at temperatures above 150° C, thermal condensation of the rubber hydrocarbon is possible. All this leads to the fact that, in mixtures based on sodium-butadiene rubber, a maximum is observed only on the kinetic curves representing variations in strength (Figure 7). Even a mixture with 2 per cent of sulfur shows no minima on the swelling or relative elongation curves. Characteristic, too, is the fact that the

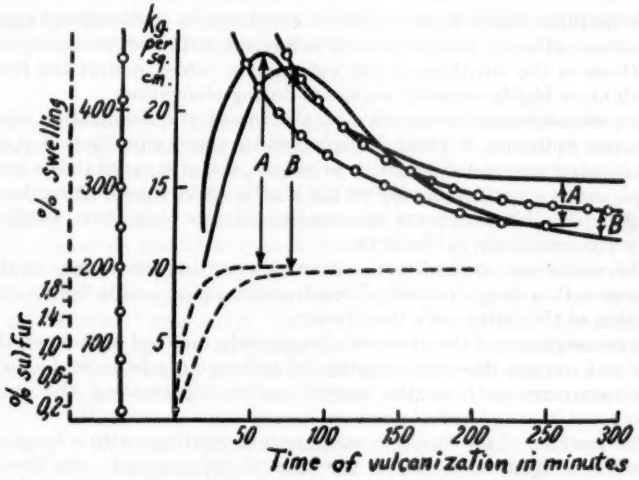

FIG. 7.—Kinetics of vulcanization of sodium-butadiene rubber mixtures containing 2 per cent sulfur
A—Mercaptobenzothiazole. B—Diphenylguanidine.

strength maximum appears considerably later than the instant in which the sulfur is completely exhausted. This indicates beyond doubt that the decrease in strength in this case occurs because of the formation of a denser space lattice, or because of continued reaction with oxygen, or else because of thermal condensation. In cases in which the sodium-butadiene mixtures do not contain enough constructive agents to form a sufficiently dense lattice, the maximum on the strength curve either fails to appear or else appears inconspicuously and only if the rate of deformation is very high.

Note on methods.—All curves were plotted on the basis of experimental data obtained with mixtures of the composition shown in Table 1. The mixtures were prepared on a mill in the usual manner, and were vulcanized in a press. Mechanical properties were determined with a Schopper dynamometer, no less than sixteen samples being taken for each point. Combined sulfur was determined by Bolotnikov's method. Swelling was conducted in Dogadkin's

TABLE 1

COMPOSITION OF TEST MIXTURES

Components	High sulfur mixtures			Low sulfur mixtures			
Smoked sheet rubber	100	100	100	100	100	—	—
Sodium-butadiene rubber	—	—	—	—	—	100	100
Sulfur	7	7	7	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Mercaptobenzothiazole	—	0.3	—	0.6	—	0.6	—
Diphenylguanidine	—	—	0.378	—	0.756	—	0.756

apparatus. The procedure used for x-ray analysis and for calculating the crystalline phase in the vulcanizate was that previously described by Lukin and Kasatochkin[3].

CONCLUSIONS

1. In mixtures with a large content of constructive (vulcanizing) agent, the vulcanization-optimum phenomenon is connected with the formation of dense space-lattices in the structure of the vulcanizate, which inhibit the formation of crystalline or highly oriented segments during elongation.

2. In contrast to mixtures with a small content of vulcanization agent, the vulcanization optimum of which is explained by superimposition of oppositely directed constructive and destructive processes, the case noted in the preceding paragraph shows a maximum only on the kinetic curve representing the change in strength. The kinetic curves representing relative elongation, swelling, and solubility are monotonic in character.

3. The maximum on the kinetic curve representing the change in strength in mixtures with a large content of constructive agent occurs before complete combination of the latter with the rubber.

4. In consequence of the absence of oppositely directed actions on the part of sulfur and oxygen, the vulcanization of sodium-butadiene rubber mixtures shows a maximum only on the kinetic curves representing the change in strength.

5. The position of the strength maximum in mixtures with a large content of constructive agent depends on the rate of deformation. As the rate of deformation is decreased, the maximum appears after more prolonged vulcanization periods of the mixtures.

6. The strength of natural rubber vulcanizates at the vulcanization optimum is a linear function of the quantity of crystalline phase formed during elongation.

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DEPENDENCE OF ELASTIC PROPERTIES OF VULCANIZED RUBBER ON THE DEGREE OF CROSS-LINKING *

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INTRODUCTION

The network-statistical theory of rubber elasticity leads to the following expression for the force of retraction in stretched rubber as a function of temperature, elongation, and network structure[1]:

$$\tau = RT(\nu/V)(\alpha - 1/\alpha^2) \qquad (1)$$

where T is the absolute temperature, ν is the effective number of chains[2] extending between cross-linkages within the volume V of the rubber, α is the length of the stretched rubber relative to its unstretched length, and τ is expressed as the retractive force per unit initial cross-sectional area. That the contribution of the heat term, omitted from consideration in Equation (1), is generally negligible has been abundantly verified by the observed proportionality between the retractive force (at constant α) and the absolute temperature[3]. The function of α occurring in Equation (1) fails to depict accurately the shape of the actual stress-strain curve, but it affords a rough approximation to it in some cases[4]. Perhaps the most significant feature of the above relationship, and the one with which we are mainly concerned here, is the predicted dependence of the retractive force on the structure of the network as embodied in the factor ν/V. With rare exceptions, previous investigations on the elastic properties of vulcanized rubberlike materials have been conducted on specimens of indeterminable network structure. Hence the validity of the proportionality between force of retraction and effective number of network elements (chains) predicted by the statistical theory of elasticity of network structures has not been subjected heretofore to experimental test[5].

The effective number ν of chain elements generally depends primarily on the numbers of cross-linkages introduced in the formation of the network. Conventional vulcanization of rubber with sulfur and accelerators is a complex process, and more than one type of cross-linkage may be formed[6]. Reliable analytical determination of the total number of cross-linkages in sulfur vulcanizates does not appear to be feasible at the present time.

Recently developed[7] disazodicarboxylate vulcanizing agents react quantitatively with rubber, one cross-linkage being introduced for each mole of the reagent. Through the use of these compounds, rubber vulcanizates characterized by known degrees of cross-linking may be readily prepared, and hitherto

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unexplored relationships between various physical properties and vulcanizate structure may be explored. The present investigation has been devoted primarily to the experimental determination of the dependence of the force of retraction on the degree of cross-linking in rubbers vulcanized in this manner.

THEORETICAL

To express the "structure factor" ν/V in more tangible form, the effective number ν of chains must be related to directly measurable quantities. Consideration of the network structure leads to the relationship[2]:

$$\nu = \nu_0 - 2N$$

where N is the number of primary molecules (*i.e.*, polymer molecules present before the introduction of cross-linkages) and ν_0 is half the number of cross-linkages within the volume V. The indeterminate number of intramolecular "short circuit" connections should be deducted from the above expression, but otherwise it should be valid with slight approximation. On introducing this expression for ν into Equation (1), the elasticity equation can be expressed in either of the alternate forms:

$$\tau = (RT/V_u)(\rho - 2/x)(\alpha - 1/\alpha^2) \tag{2}$$

or:

$$\tau = (RTd/M_c)(1 - 2M_c/M)(\alpha - 1/\alpha^2) \tag{3}$$

where ρ is the "density" of cross-linked units, or fraction of the structural units which are cross linked, V_u is the volume of one unit, x is the degree of polymerization, M is the molecular weight (number average) of the primary rubber molecules, M_c is the molecular weight per cross-linked unit, and d is the density of the vulcanizate. Thus:

$$\nu_0 = \rho V/V_u = Vd/M_c$$

and:

$$N = V/xV_u = Vd/M$$

The linear dependence of τ on the reciprocal of the primary molecular weight M at fixed α and constant density ρ of cross-linked units has been confirmed in the case of Butyl rubber[3], which is particularly amenable to this type of experiment. The magnitude of the force of retraction, however, was observed to be about three times that predicted by the above theoretical equations. It was suggested that entanglements of chains may be responsible for the enhancement of $\tau_{obs.}$ as compared with the calculated value. The further suggestion was made that entanglements in Butyl rubber vulcanizates may be excessive, owing to the peculiar nature of vulcanization when so few reactive units are present.

The theoretically predicted influence of degree of cross-linking on τ at constant primary molecular weight M is more clearly shown by Equation (2). The linear relationship differs from a simple proportionality merely by the term $2/x$, which can be made almost negligible by employing polymers of high molecular weight. Results on Butyl rubber indicated a slower increase of τ with ρ than predicted by theory, a result which appears to be in line with the postulate that entanglements contribute appreciably to the restraints on the deformed structure. However, the range of ρ values covered in these experiments was too small for a definite decision on this point.

EXPERIMENTAL

MATERIALS

The synthesis of the disazodicarboxylates:

$$(RO—CO—N{=}N—COO)_2R'$$

is described elsewhere[7]. Decamethylene dis-methylazodicarboxylate [10–1][9] was prepared by nitric acid oxidation of the corresponding bishydrazo compound; hypochlorous acid oxidation was employed in preparing decamethylene dis-*n*-decylazodicarboxylate [10–10]. Both were purified by recrystallization from a mixture of ethyl acetate and hexane to constant melting points, 38–39° and 35–36°, respectively. While analytical data[7] were otherwise satisfactory, the latter [10–10] contained a trace of halogen. The [10–1] compound was stable for months at room temperature, whereas the [10–10] compound decomposed slowly on standing, the initially crystalline material changing to an oil in the course of several months. Diethylene disethylazodicarboxylate [5–2], an oil which cannot be distilled, was prepared by nitric acid oxidation of the hydrazo intermediate. Since it could not be purified, its use was restricted to preliminary explorations.

Stock solutions of natural rubber containing about 5 per cent of rubber in benzene were prepared from pale crepe which had been subjected to slight breakdown by 15 passes between mill rolls. The solutions were prepared at room temperature, filtered with pressure, and stored in the dark.

GR-S synthetic rubber containing 72 per cent butadiene was dissolved in benzene and precipitated with alcohol for the purpose of eliminating extraneous substances of low molecular weight. Approximately 1 per cent of phenyl-β-naphthylamine was added to the precipitate before drying in vacuum at 60°. Stock solutions were prepared containing about 10 per cent of the purified GR-S in toluene. More uniform GR-S films could be cast from this solvent than from benzene. In spite of their higher concentrations, the GR-S solutions were less viscous than the rubber stock solutions.

Concentrations of the stock solutions were accurately determined by evaporating weighed samples to dryness and weighing the residues. Intrinsic viscosities, measured on diluted portions of the stock solutions, were about 4.5 and 2.0 for the natural rubber and GR-S, respectively. These values correspond to viscosity average molecular weights of 950,000 and 225,000, respectively[10].

PREPARATION OF VULCANIZATES

A small quantity of the benzene solution containing the required amount of the disazodicarboxylate was mixed thoroughly with a weighed portion of the stock solution of rubber. The solution was subjected to vacuum for the purpose of removing gas bubbles and dissolved gases. It was then poured onto a glass tray consisting of a rectangular piece of plate glass provided around its edges with vertical barriers made of glass strips cemented to the plate glass. The tray was placed, carefully levelled, in a ventilated oven where it was heated at 60° for two hours. The vulcanized rubber sheet was then stripped from the tray. With proper manipulation, bubble-free, unrippled sheets could be obtained. Thicknesses ranged from 2 to 14 mils (inches $\times 10^3$), depending on the quantity of rubber used. Edges of the sheets were excessively thick, but elsewhere the sheets were fairly uniform in thickness, although not accurately so.

MEASUREMENT OF THE FORCE OF RETRACTION

Forces were measured with a triple beam balance sensitive to 0.01 gram. The weighing pan was removed and a vertically adjustable platform was mounted on the base of the balance directly under the stirrup. The apparatus, exclusive of the balance, is shown diagrammatically in Figure 1. A two-inch rubber stopper A to which the lower test clamp C was fastened, was anchored, small end up, to the adjustable platform B. The rubber stopper served as the support for a 2 × 5-inch glass tube D which surrounded the sample during equilibration (see below) and measurement of the force of retraction. A thin rubber stopper E was inserted in the upper end of the glass tube. Through a small hole in the center of this stopper a fine wire F connected the upper test clamp C′ to the stirrup of the balance directly above the tube. Another hole G in the upper stopper provided for the addition and removal of equilibrating liquids.

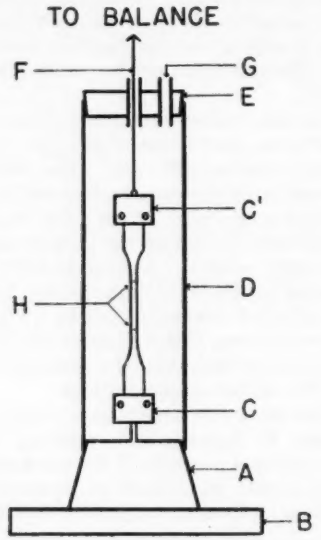

FIG. 1.—Diagram of apparatus for measuring force of retraction.

A small dumbbell test-specimen was cut from the vulcanized rubber sheet, using a die having dimensions similar to those described previously for micro-testing of rubber[8]; the mid-section is 0.100 inch wide and 0.5 inch long. A pair of ink marks H, about 1 cm. apart, was carefully placed within the uniform section of the dumbbell and the ends of the dumbbell were fastened in the clamps. The clamps consisted merely of pairs of aluminum plates with approximate dimensions 1.0 × 1.5 × 0.3 cm., each pair being held together by two screws. The end tab of the dumbbell was held between these plates under the pressure provided by the screws.

After fastening the sample in the clamps, the glass tube was put in place about the sample, the wire attached to the upper clamp was inserted through the upper stopper and attached to the balance stirrup, and the upper stopper was set in place. The platform supporting the lower rubber stopper and clamp

was lowered gradually until the balance reached zero position at substantially zero load on the test-piece. The balance arm was locked at this point and the distance between centers of the ink marks was read with a travelling microscope reading to 0.002 inch. The platform was then lowered until the desired elongation was reached, as observed with the travelling microscope in the same manner.

The method used for equilibration is similar to that described by Gee[11]. The glass tube surrounding the test sample was filled with petroleum ether (b.p. 30–60°) and swelling allowed to proceed for about ten minutes. The petroleum ether was then removed and air or nitrogen was passed through the tube for about forty minutes to complete evaporation of all petroleum ether absorbed by the sample. The balance arm was then unlocked and the force observed. All measurements reported here were carried out at about 25° C.

The distance between the ink marks, when remeasured in several instances following the swelling cycle, was found to remain unaltered by the treatment with petroleum ether. The force, however, was appreciably less, the greater change occurring in samples of low degrees of cross-linking.

TABLE I

EQUILIBRATION OF NATURAL RUBBER [10–1] VULCANIZATES AT 100 PER CENT ELONGATION

$\rho \times 100$, equiv. % of [10–1]	τ before equilibration (lb. per sq. in.)	Time after equilibration treatment (hours)	τ after equilibration (lb. per sq. in.)
0.10	27	0.5	14.0
		1.0	13.8
		3.	13.6
		16.	13.1
		24.	13.0
0.20	34	0.25	26.6
		1.0	26.7
1.00	85.3	0.25	83.5
		0.50	83.8
		1.25	83.7

Our observations confirm those of Gee pertaining to the adequacy of the above treatment for arriving at values for the force of retraction τ, which are true equilibrium values characteristic of the vulcanizate network structure. Without solvent equilibration the stress continues to relax over an indefinitely long period; the value of τ arrived at in this manner is strongly dependent on the patience of the investigator. After the solvent equilibration treatment, on the other hand, the force of retraction remains constant for many hours. Typical results are shown in Table I. Even at the lowest degree of cross-linking where the average distance between cross-linking points is a thousand structural units, a remarkably stable equilibrium value is secured, this value being much lower than the force observed prior to equilibration. The initial force of retraction exceeds the equilibrium value by an amount which diminishes rapidly as the degree of cross-linking is increased. Thus, the equilibration operation becomes unimportant for higher values of ρ. In agreement with Gee's findings, the same equilibrium value for τ at 100 per cent elongation was obtained when the rubber was first stretched to a higher elongation, equilibrated, allowed to retract to the chosen elongation, *e.g.*, 100 per cent and again equilibrated.

Following the elasticity measurements, the sample was relaxed to its initial length and a 1.00-cm. segment of the mid-section of the dumbbell was accurately cut out with a die. This rectangular segment, 0.254 cm. in width and 1.00 cm. long, was weighed to the nearest 0.01 mg., and the thickness and cross-section were computed from the weight, assuming a density of 0.92.

SULFUR ACCELERATOR VULCANIZATES

For comparison of elastic properties, thin natural-rubber sheets were vulcanized with sulfur and accelerator, using the following recipe.

Pale crepe	100.	Stearic acid	1.0
Sulfur	2.5	Zinc oxide	5.0
Mercaptobenzothiazole	0.75		

SWOLLEN SAMPLES FOR ELASTICITY MEASUREMENTS

For the purpose of exploring the influence of swelling on elastic properties of azo-vulcanized rubbers in comparison with the effect of swelling agents on rubber vulcanized with sulfur and accelerator, weighed dumbbell specimens were placed in mineral oil (Nujol) for such times as were required for imbibition of the desired proportion of the swelling agent. The specimen was then removed from the mineral oil and allowed to stand overnight to assure uniform distribution throughout the sample. After reweighing, the force of retraction was measured; equilibration was unnecessary because the swelling agent assures rapid attainment of equilibrium.

Determination of swelling ratio.—A small section (about 0.1 gram) of the vulcanized rubber sheet was weighed accurately and placed in benzene containing 1 gram per liter of phenyl-β-naphthylamine. As a further precaution against degradation, swelling was carried out in darkness. Preliminary tests indicated that equilibrium was obtained within five hours.

When this point was reached, the sample was transferred to a small tube carrying a 19/38 ground glass joint. This was attached to a stopcock which was connected through a 10/30 ground joint to a T-tube. One arm of this tube led to a reservoir of benzene, the other to a vacuum pump. The system was evacuated to 20-mm. pressure and placed in a constant temperature bath at 25° for a half hour to establish equilibrium. The stopcock to the sample tube was closed, the vacuum in the remainder of the system broken, and the sample tube plus stopcock connection removed and weighed. The sample was then taken out and the tube (containing droplets of benzene) reweighed. By this procedure it was possible to obtain the weight of the swollen sample in a saturated benzene atmosphere, thus eliminating the loss of weight due to evaporation of the benzene. A blank was carried out to determine the difference in weight between the sample tube containing the benzene atmosphere and the same containing air. This correction was applied to the weight of each sample.

Five samples were measured from each vulcanizate and an average of the values was taken.

RESULTS

PRELIMINARY CONSIDERATIONS

The pure disazodicarboxylates, when incorporated in rubber in the manner described above, are believed to introduce cross-linkages in substantially the stoichiometric amount for reasons which may be set forth as follows:

(1) Ethyl azodicarboxylate reacts with rubber[12] and with the analogous monomeric unsaturate compound, trimethylethylene[7], giving in each case a quantitative yield of the adduct. If an excess of either hydrocarbon is used, all nitrogen of the ethyl azodicarboxylate is combined in the adduct produced. The structure of the one-to-one adduct formed with trimethylethylene has been established[7].

(2) The [10–1] disazo compound adds quantitatively with trimethylethylene, present in excess, to form a stable adduct. This product is an oil which could not be distilled up to 300° C at a pressure of 1 mm. Its structure has not been established, but it is presumed to be analogous to the ethyl azodicarboxylate-trimethylethylene adduct.

(3) The elastic properties of the azo-vulcanized rubbers are insensitive to the temperature and time of heating, provided they are adequate for completion of the addition. The properties of vulcanizates prepared by casting films from different solvents are the same.

TABLE II

FORCE OF RETRACTION AS A FUNCTION OF CONDITIONS OF VULCANIZATION[a]

Solvent	Temperature (° C)	Time (hours)	r at 100% elongation (lb. per sq. in.)
Benzene	60	2	48.9
Benzene	60	2	50.7
Benzene	60	2.5	47.1
Benzene	60	3	50.9
Benzene	60	3.5	51.1
Toluene	60	2	50.4
Carbon tetrachloride	60	2	50.2
Benzene	40	3	64.4[b]
Benzene	70	1.5	66.0[b]

[a] All natural rubber vulcanizates prepared using 1.0 equivalent per cent of [5–2].
[b] A different, apparently purer, preparation of the [5–2] equivalent compound was used in these two experiments.

Preliminary results such as those shown in Table II indicated the adequacy of two hours at 60° for completion of the addition reaction. Different preparations of the [5–2] disazo-vulcanizing agent used in these experiments gave discordant results, owing to the variable purity of this compound. Sets of results obtained by using the same batch of vulcanizing agent provide the necessary information, however. Further use of the 5–2 compound was abandoned in favor of the [10–1] and [10–10] compounds, which may be obtained in crystalline form. Similar, though less complete, exploratory experiments demonstrated that 2 hours at 60° was also sufficient for vulcanization with the [10–1] compound. It was found further that films prepared by casting a solution of natural rubber and [10–1] in the low-boiling solvent, ethyl bromide, followed by heating for 1 hour or more at 60° exhibited tensile strengths and ultimate elongations agreeing closely with values obtained using benzene as solvent. GR-S reacted with the azo compounds at a similar rate.

It would be difficult, if not impossible, to demonstrate in a straightforward manner by any presently known technique whether or not chain scission accompanies the cross-linking process. That the primary rubber molecules survive the azo-vulcanizing process without excessive degradation is indicated, however, by the rather small change in intrinsic viscosity occurring when rubber films are prepared according to the standard procedure, using small pro-

TABLE III

EFFECTS OF ETHYL AZODICARBOXYLATE (EAD) ADDITION ON THE INTRINSIC VISCOSITY OF NATURAL RUBBER[a, b]

Equiv. % EAD	Intrinsic viscosity in benzene	$\bar{M}_v \times 10^{-3}$ calculated[c]
0	5.09	10
2	4.70	9.2
4	2.96	4.6
8	2.92	4.5

[a] All films cast from benzene solutions containing EAD, then dried at 60° for 2 hours.
[b] The intrinsic viscosity of the rubber in the stock solution was 5.26.
[c] The viscosity average molecular weight values given in the last column are viscosity averages calculated from the relationship of Carter, Scott, and Magat[13] for rubber in toluene; intrinsic viscosities for rubber in benzene and in toluene are similar.

portions of ethyl azodicarboxylate in place of the disazo compound. These results are shown in Table III. The rather marked decrease in intrinsic viscosity when larger proportions are used must be caused, in part at least, by the chemical modification of the polymer chain resulting from formation of the adduct. Benzene is a poor solvent for the modified rubber chains, hence the intrinsic viscosity is diminished on this account. The molecular weight values for the more highly modified rubbers included in Table III may be considerably too low for this reason.

EFFECT OF SAMPLE THICKNESS

The retractive force per unit cross-section at a given elongation was observed to vary somewhat with the thickness of the sheet, as shown by the results plotted in Figure 2. The effect appears to vanish for low proportions of the vulcanizing agent, and with higher proportions it becomes small, below a thickness of about 5 mils. Sulfur vulcanizates exhibited τ values independent of thickness. Four rubber sheets varying from 12 to 25 mils in thickness but otherwise identically prepared by vulcanizing in a press for 30 minutes at

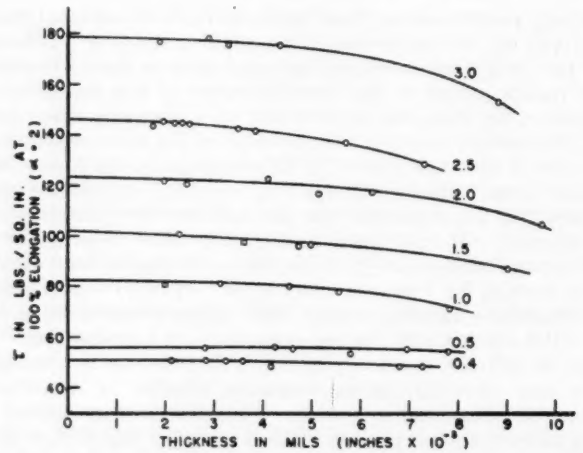

FIG. 2.—Force of retraction τ *vs.* thickness of vulcanized sheets for the various proportions of [10–1] vulcanizing agent indicated by the equivalent percentage figures ($\rho \times 100$) adjacent to each curve.

285° F using the sulfur-mercaptobenzothiazole recipe given above registered identical values for τ at 100 per cent elongation.

The possibility that the above behavior of the azo vulcanizates is related to the occurrence of partial vulcanization before evaporation of solvent appears to be ruled out by the uniformity of results obtained with different solvents (see below). We are inclined to attribute the observed dependence of properties on thickness to the limited compatibility of the disazo-vulcanizing agents with rubber; when the proportion of the azo compound is large, it may tend to segregate (although not visibly so) on the surface and, if the sheet is thick, diffusion may be too slow to assure uniform reaction throughout. On the other hand, an appreciably "tighter cure" on one surface than on the other is rendered unlikely by the observation that samples swollen in solvents show no tendency to curl.

Whatever may be the cause of the variation in elastic properties with thickness, the magnitude of the effect is not large and approximately constant values for τ are observed for all thicknesses below 5 mils. Extrapolation to zero thickness offered the best means for minimizing the influence of the anomaly.

THE STRESS-STRAIN RELATIONSHIP

The stress in conventionally vulcanized rubber is known to depend on the relative length α in a manner which is approximated only roughly by the function of α occurring in the alternate Equations (1) to (3) derived from the network-statistical theory of rubber elasticity[14]. The departure of the stress dependence on elongation from theory has been shown in a particularly effective manner by Gee[15], who calculates a quantity designated as χ which is proportional to the ratio of the observed force of retraction $\tau_{obs.}$ to that calculated from Equation (1). Modifying Equation (1) to include networks swollen with diluent after vulcanization:

$$\tau = RT(\nu/V)(\alpha - 1/\alpha^2)/v_2^{1/3} \tag{4}$$

where α is ratio of the length of the stretched, swollen sample to unstretched, swollen length and v_2 is the volume fraction of polymer (rubber) in the swollen sample. Then χ is defined by Gee as follows:

$$\begin{aligned} \chi &= (\tau_{obs.}/\tau_{calcd.})(V/R\nu) \\ &= \tau_{obs.}/[T(\alpha - 1/\alpha^2)/v_2^{1/3}] \end{aligned} \tag{5}$$

Whereas, according to theory, χ should be a constant for a given vulcanizate Gee observed that it decreased with increase in α in all cases investigated, including gum vulcanizates of various synthetic rubbers as well as natural rubber. He also showed that χ tends to decrease on swelling, the change in χ with α for swollen rubbers being small.

In Figure 3 the magnitude of the variation of χ with α for azo-vulcanized rubbers is seen to be roughly independent of the extent of cross linking. Considered from the standpoint of the percentage variation of χ with α, the effect is relatively unimportant at high degrees of cross-linking but excessively so at very low degrees. When $\rho = 0.10$, for example (results not shown in Figure 3), the effect is manifested by an increase of only about 10 per cent in τ between $\alpha = 2$ and 3. At high degrees of cross-linking the data suggest that χ passes through a minimum value beyond which it increases with further elongation.

The effects of a diluent (Nujol) on χ, shown in Figures 4 and 5, parallel the

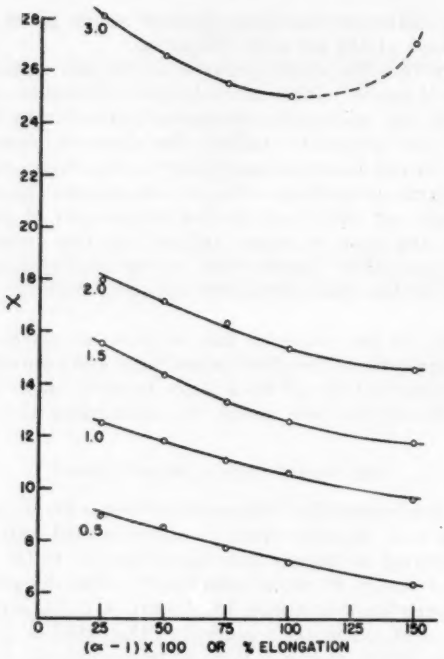

FIG. 3.—Relative stress dependence on elongation. χ, representing a quantity proportional to $f_{obs.}/r_{reduced}$, plotted against the relative extension α for the degrees of cross linking ($\rho \times 100$) indicated with each curve.

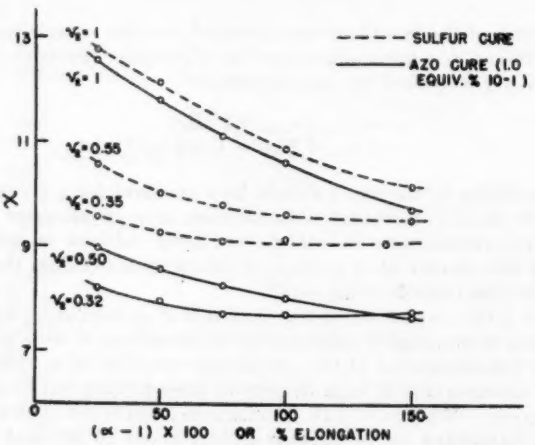

FIG. 4.—Relative stress dependence on elongation for azo- and for sulfur-vulcanized natural rubber swollen to the various degrees indicated for each curve. (Swelling-volume ratio = $1/v_2$.)

observations of Gee on sulfur vulcanizates. The displacement of χ with addition of diluent seems to be greater for the $\rho = 1.00 \times 10^{-2}$ azo vulcanizate than for the sulfur-accelerator vulcanizate (30 minute cure at 285° F) shown for comparison. The results obtained for somewhat higher degrees of cross-linking ($\rho = 1.5$ and 2.0×10^{-2}) exhibit a smaller change of χ with swelling, which is more in line with the sulfur vulcanizate results. The conclusion appears justified that the elastic properties of the azo vulcanizates do not differ significantly from those of rubbers vulcanized in the conventional manner to similar degrees of cross-linking.

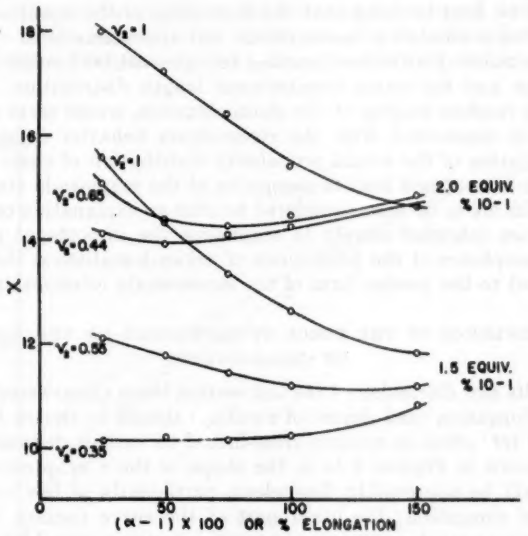

FIG. 5.—Relative stress dependence on elongation for higher azo vulcanizates swollen to the various degrees indicated.

The cause of the deviation of $\tau_{obs.}$ from its theoretically predicted dependence on ρ and degree of swelling ($1/v_2$), as demonstrated by the variation in χ is not clear. As Gee pointed out, the swollen rubbers behave more nearly in accordance with theory than the unswollen rubbers, and χ for the latter at higher elongations approaches the fairly constant value assumed by χ for the highly swollen samples. These observations led Gee[15] to conclude that a swollen and (or) stretched ($\alpha \cong 2$) rubber behaves approximately ideally and that the unswollen vulcanizate at low elongation deviates most widely from ideality. Gee's suggestion that this deviation is caused by a tendency for the rubber chains to assume a condition of alignment, this tendency being enhanced by elongation and depressed by swelling, is untenable from either of two points of view. On purely thermodynamic grounds, no system spontaneously tends toward a more ordered state unless this state offers a lowering of internal energy. Thermoelastic measurements, however, show that the internal energy of the rubber is very nearly independent of the elongation. Secondly, if Gee's explanation were correct, the anomaly in χ would surely be widely variable among various types of rubbers. Gee's results show that this is not the case.

Pasternak and Kuhn[16] recently observed that the elastic modulus of vulcanized rubber at small extensions decreases more rapidly with swelling than theory would predict. This observation is equivalent to the decrease in χ discussed above for somewhat greater extensions. They attributed the deviation from theory to secondary bonds between chains, these bonds acting to increase the degree of cross-linking in the unswollen rubber, but being broken in the presence of the swelling agent. This conclusion appears to be untenable inasmuch as equilibration by temporarily swelling the unswollen samples in the above manner does not eliminate the discrepancy between χ values for the swollen and unswollen samples.

It should be kept in mind that the derivation of the equation of state for rubber rests on a number of assumptions and approximations. Of these, the use of the Gaussian distribution function to represent both relative numbers of configurations and the chain displacement length distribution, and the disregard of the random lengths of the chain elements, would seem to be of likely significance in connection with the stress-strain behavior considered above. A minor deviation of the actual probability distribution of chain lengths from the Gaussian form would lead to anomalies of the magnitude observed above. These remarks are in no wise considered to offer an explanation of the observations; they are intended merely to emphasize the importance of avoiding a too-literal acceptance of the predictions of network-statistical theory, particularly in regard to the precise form of the stress-strain relationship.

DEPENDENCE OF THE FORCE OF RETRACTION ON THE DEGREE OF CROSS-LINKING

The results and discussion of the last section leave unanswered the question as to what elongation (and degree of swelling) should be chosen for comparing the forces of retraction in rubbers cross-linked to various degrees. According to results shown in Figures 3 to 5, the shape of the τ *vs.* ρ curve at a given elongation will be appreciably dependent, particularly at low values of ρ, on the choice of elongation; the lower part of the curve (near $\rho = 0.2 \times 10^{-2}$) may be altered as much as 50 per cent relative to the upper (high ρ) end of the curve, depending on the elongation at which the comparisons are made.

Somewhat arbitrarily, but in part for the sake of experimental convenience, we have chosen 100 per cent elongation ($\alpha = 2$) for this purpose. Results obtained with natural rubber vulcanizates prepared using various proportions of the [10–1] disazo compound are shown in Table IV. Most of the values

TABLE IV

FORCE OF RETRACTION AT 100 PER CENT ELONGATION AND DEGREE OF CROSS-LINKING; NATURAL RUBBER VULCANIZED WITH [10–1]

Equiv. % of [10–1] ($\rho \times 100$)	Sheet thickness (mils)	τ (lb. per sq. in.)
0.10	16.5	13.5
0.20	11.0	26.7
0.40	Extrapolated to zero	50
0.50	Extrapolated to zero	55
0.80	9.6	69
1.00	Extrapolated to zero	82
1.50	Extrapolated to zero	102
2.00	Extrapolated to zero	124
2.50	Extrapolated to zero	147
3.00	Extrapolated to zero	178

represent extrapolations to zero thickness from the results shown in Figure 2. There extrapolation was not employed, the proportions of vulcanizing agent for the first two samples are small enough to obviate the need for extrapolation.

These characteristic τ values for $\alpha = 2$ are plotted against ρ in Figure 6. The broken straight line represents the theoretical relation according to Equation (2), assuming $2/x = 0$. The actual value of x (number average) may be assumed to be at least 5000. Hence $x/2$ is all but negligible in Equation (2), and the required displacement of the intercept of the theoretical line from the origin in Figure 6 should be barely perceptible. Also included in Figure 6 are average τ values for rubber vulcanizates prepared by using the [10–10] disazo compound. The results on which these averages are based were erratic, presumably due to the instability of our sample of this vulcanizing agent. The accuracy of this set of points is, therefore, questionable, and no significance is

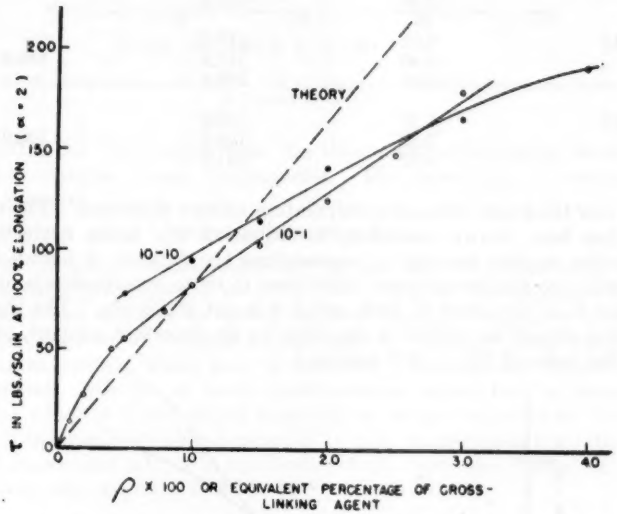

FIG. 6.—Dependence of the force of retraction on degree of cross linking for natural rubber vulcanizates.

attached to the fact that they are in general somewhat higher than the much more reliable values for the [10–1] vulcanizates[17]. Over most of the range, τ for a given proportion of cross-linking agent, appears to be approximately independent of the particular agent selected.

Observed magnitudes for τ on the whole are remarkably close to the predictions of theory. The change in τ with ρ is less than predicted, however, τ being higher than theory for low degrees of cross-linking, while the reverse is true at high degrees. The nature of the variation of χ with α (Figure 3) makes clear that this deviation could not be appreciably reduced by choice of an α other than 2 for the force measurements; if a lower α were chosen, this deviation would be enhanced somewhat.

Corresponding results on the dependence of τ at $\alpha = 2$ on ρ for GR-S vulcanized with 10–1 are given in Table V and Figure 7. ρ is expressed in equivalents per butadiene unit. In most cases the values represent measure-

TABLE V

FORCE OF RETRACTION AT 100 PER CENT ELONGATION AND DEGREE OF CROSS-LINKING; GR-S VULCANIZED WITH [10–1]

Equiv. % of [10–1] ($\rho \times 100$)	Sheet thickness (mils)	τ (lb. per sq. in.)	τ (average)
0.50	3.81	61.3	
	3.81	61.1	61.4
	3.67	61.7	
1.0	6.02	83.1	
	5.04	83.6	83.2
	7.10	83.0	
1.5	5.91	121.0	
	4.34	123.0	121.8
	3.97	121.3	
2.0	6.01	147.9	
	5.80	147.9	148.0
	6.07	148.1	
2.5	5.27	159.9	
	5.69	158.2	160.0
	5.07	161.9	

ments at low thickness without extrapolation to zero thickness. The theoretical line has been drawn according to Equation (2), again neglecting $2/x$. Although the number average x (representing the number of butadiene units per molecule) for the precipitated GR-S used in these experiments is unknown, it probably is of the order of 1000 and $2/x$ is not negligible. The theoretical straight line should be shifted to the right by an uncertain amount, presumed to be of the order of 0.2×10^{-2} unit in ρ.

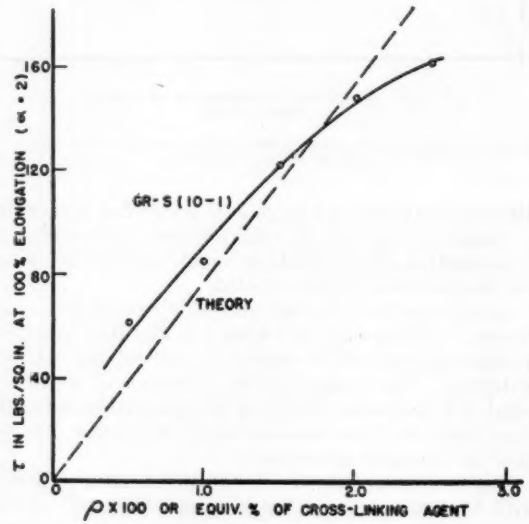

FIG. 7.—Dependence of the force of retraction on degree of cross-linking for GR-S vulcanizates.

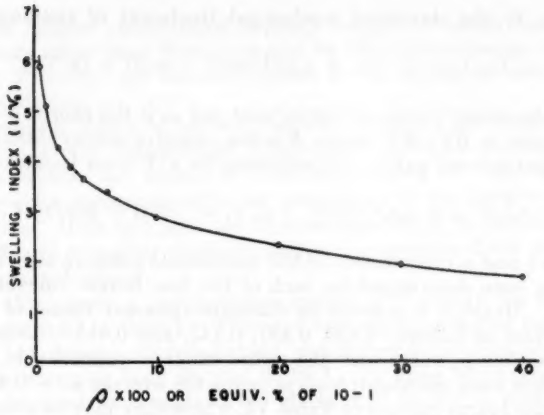

FIG. 8.—Swelling-volume ratio ($SV = 1/v_2$) *vs.* degree of cross-linking for natural rubber in benzene at 25° C.

The results for GR-S agree witl the theory somewhat better than is the case for the natural rubber vulcanizates. The same type of deviation is apparent, however.

EQUILIBRIUM SWELLING

Force of retraction measurements at 100 per cent elongation could not be extended satisfactorily beyond $\rho = 3 \times 10^{-2}$ owing to the tendency of more highly cross-linked samples to tear at the test clamps. Response of the vulcanizate structure to deformation may also be adduced from equilibrium swelling measurements, which may be extended to considerably higher degrees of cross-linking. Results of such measurements carried out in benzene on samples for which $\rho \times 10^2$ varied from 0.5 to 40 are recorded in Table VI. In Figure 8 the swelling-volume ratio $SV = 1/v_2$, representing the ratio of the volume of the swollen sample at equilibrium to its unswollen volume, is plotted against ρ over the range 0.5 to 20×10^{-2}.

TABLE VI

EQUILIBRIUM SWELLING OF NATURAL RUBBER [10–1] VULCANIZATES IN BENZENE AT 25° C

$\rho \times 10^2$	$SV = 1/v_2$	$\tau_{obs.}$ at 100% elongation (lb. per sq. in.)	τ^a at 100% elongation calcd. from swelling	τ^b at 100% elongation calcd. from theory
0.50	5.89	55	58	42
1.00	5.11	82	82	83
2.00	4.27	124	128	161
3.00	3.88	178	163	235
4.00	3.66		190	305
6.00	3.40		230	435
10.0	2.87		370	660
20.0	2.31		700	1070
30.0	1.94		1280	1360
40.0	1.71		1860	1560

[a] Calculated from equilibrium swelling volume ratio ($1/v_2$), using Equation (7) with $\mu_1 = 0.430$ and for $\alpha = 2$.

[b] Calculated from elasticity theory according to Equation (8).

According to the statistical mechanical treatment of swelling[18], at equilibrium:

$$-[\ln(1-v_2)+v_2+\mu_1 v_2^2]/(v_2^{1/3}-v_2/2)=(\nu/V)V_1 \qquad (6)$$

where V_1 is the molar volume of the solvent and μ_1 is the energy of interaction parameter equal to BV_1/RT, where B is the cohesive energy density constant for the polymer-solvent pair[19]. Substituting for ν/V from Equation (1):

$$-[\ln(1-v_2)+v_2+\mu_1 v_2^2]/(v_2^{1/3}-v_2/2)=[\tau/(\alpha-1/\alpha^2)](V_1/RT) \qquad (7)$$

which relates τ and v_2 independent of the vulcanizate network structure. Both τ and v_2 have been determined for each of the four lowest vulcanizates listed in Table VI. Hence it is possible to calculate apparent values of μ_1 for each of these samples as follows: 0.438, 0.431, 0.435, and 0.415. Although application of the same μ_1 value over the entire range is questionable, equivalent values of τ have been calculated from v_2, using the average $\mu_1 = 0.430$. These are given in the fourth column of Table VI, where they may be compared with the observed τ values given in the third column and with those in the last column calculated from the degree of cross-linking according to theory. The alternate Equation (3) has been used for this purpose, neglecting the inconsequential $2M_c/M$ term and making allowance for the relatively large weight fraction of the vulcanizing agent in the higher vulcanizates through the use of the relationship:

$$M_c = 68/\rho + 402/2$$

where 402 represents the molecular weight of the [10–1] disazo compound. Assuming the same density, 0.92, for all vulcanizates:

$$\tau_{\alpha=2} = 5.8 \times 10^5/(201 + 68/\rho) \qquad (8)$$

from which figures in the last column of Table VI have been calculated.

The τ values computed from the swelling measurements (column four) may deviate appreciably from the actual forces of retraction which, if measurable, would be exhibited by the higher vulcanizates. A moderate decrease in μ_1 with increase in ρ in the intermediate range is indicated. This would lead to somewhat larger values for the τ values calculated from swelling in this range. At the highest degrees of cross linking, μ_1 must increase owing to the increasing polar character of the polymer resulting from the large percentage of azodicarboxylate content. The τ values calculated from swelling data on the last two or three samples may for this reason be much too large; hence comparisons here may be of little significance. In spite of these limitations, the data in Table VI serve to show that the force of retraction continues to increase with ρ over a much wider range than was ascertainable from direct measurement of τ.

CONCLUSIONS

The results reported above demonstrate a progressive increase in the force of retraction τ at fixed elongation with increase in the fraction ρ of the structural units which are cross-linked from $\rho = 0.10 \times 10^{-2}$ to 3.0×10^{-2}. Over this range, τ at 100 per cent elongation increases about thirteenfold. Swelling measurements indicate that the increase in τ with ρ continues over an additional tenfold range in ρ. Previous assertions[20] that the modulus of elasticity

of soft gum rubber vulcanizates depends largely on chain interaction and entanglements other than those imposed by the cross-linkages, and that the modulus is, therefore, not directly related to the degree of cross-linking, are without foundation.

The statistical theory of rubber elasticity expresses the force of retraction as a function of the temperature, vulcanizate structure and elongation; no arbitrary constants are involved. The magnitudes of τ for $\alpha = 2$ are in remarkably close agreement with the predictions of the theory over most of the range in ρ. This fact is of the utmost significance in confirmation of the statistical theory of rubber elasticity and of the analysis of the network structure of vulcanized rubber.

On the other hand, τ increases less rapidly with ρ than the direct proportionality prescribed by theory. Forces of retraction are higher than the theory predicts at low degrees of cross-linking, and an opposite deviation is observed for values of ρ greater than about 1×10^{-2}. Previous observations on Butyl rubber[8], vulcanized to ρ values from about 0.16×10^{-2} to 0.28×10^{-2} indicated forces of retraction (for infinite molecular weight M) which exceed by about threefold those predicted from the theory. This deviation is decidedly larger than has been observed here in the same range for ρ. A substantial part of the discrepancy observed for Butyl rubber may have arisen from failure to secure elastic equilibrium, however.

Deviations in the values of τ from theory probably originate largely from oversimplifications in the treatment of the network structure. Entanglements of the sort previously discussed[2] tend to enhance the restraints imposed on the chains when the rubber is elongated. Their percentage effect should be greatest for low degrees of cross-linking, hence the observed τ values are higher than theory at low degrees of cross-linking. "Intramolecular" cross-linkages, yielding short-circuit structures contributing nothing to the elastic reaction of the network, should become increasingly important at higher degrees of cross linking[2]. Such wastage of cross-linkages may account for the low values of τ obtained for higher ρ values.

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[5] Since this paper was written, Bardwell and Winkler (*India Rubber World* **118**, 509 (1948)) have published results of an investigation dealing with the relationship of the force of retraction at 300 per cent elongation to the degree of cross-linking in vulcanized GR-S. Vulcanization was brought about by treating GR-S latex with potassium persulfate, and the degree of cross-linking was calculated from the gel-to-sol ratio. For degrees of cross-linking up to 0.40 equivalent per cent ($\rho = 0.40 \times 10^{-2}$), which corresponds to the lower portion of the range investigated here, forces of retraction were observed to be several-fold greater than the predictions of Equation (1). The deviation is in the same direction as we have observed, but of much greater magnitude.

[6] Armstrong, Little and Doak (*Ind. Eng. Chem.* **36**, 628 (1944)) have shown that the number of cross-linkages formed when an accelerator and sulfur in the presence of a metal soap are used is closely related to the amount of metal sulfide formed. These results have been extended by Hull, Olsen and France (*Ind. Eng. Chem.* **38**, 1282 (1946)).

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[17] Since the [10–10] preparation proved to be unstable, it may have undergone appreciable decomposition during vulcanization. In analogy with decompositions of other azo compounds, free radicals are doubtless released, and these may, depending on conditions, lead to larger extends of interlinking than would have been realized by the addition reaction alone. The larger r values obtained with [10–10] compared with [10–1] may be accounted for in this manner.
[18] Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943); Kuhn, Pasternak and Kuhn, *Helv. Chim. Acta* **30**, 1705 (1947).
[19] Equation (6) differs slightly from the previously published swelling Equation (17) by the inclusion of $-v_2/2$ in the denominator term. Its effect is not large provided that v_2 is small. The deviation of this preferred relationship will be published elsewhere.
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DEPENDENCE OF TENSILE STRENGTH OF VULCANIZED RUBBER ON THE DEGREE OF CROSS-LINKING *

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INTRODUCTION

The suitability of disazodicarboxylates as quantitative cross-linking agents for the preparation of rubber vulcanizates of known degrees of cross-linking has been emphasized previously[1]. In a recent paper[2] we have presented the results of an investigation on the dependence of the equilibrium force of retraction on the elongation and degree of cross-linking of rubber and GR-S vulcanized with these compounds. The present paper reports an extension of these investigations of the relationship of physical properties of rubberlike materials to their network structure. Specifically, the tensile strength of azo vulcanized natural rubber has been explored as a function of the degree of cross-linking and of the extent of modification of the chain units.

The tensile strengths of natural rubber specimens vulcanized to various extents using sulfur alone or sulfur in conjunction with various accelerators have been investigated in considerable detail recently by Gee[3], who has emphasized the critical dependence of the tensile strength on the degree of cross-linking. Values for the latter quantity, however, were deduced indirectly from the equilibrium force of retraction using the simple proportionality relationship between force of retraction and degree of cross-linking afforded by the theory of rubber elasticity. This relationship is known to be only approximately valid[2]. Furthermore, the effects on the force of retraction of chain scission, which doubtless accompanied some of the vulcanizations to a considerable degree, were disregarded. For these reasons, Gee's values for the degrees of cross-linking occurring in his vulcanizates are only approximate estimates, and in a few cases they may be seriously in error. Nevertheless, the general character of the relationship between tensile strength and degree of cross-linking which he obtained is confirmed by our results on rubber samples quantitatively cross-linked with measured proportions of decamethylene-dismethyl azodicarboxylate.

EXPERIMENTAL

MATERIALS

The rubber designated as "high molecular weight" consisted of pale crepe which had been subjected to 15 passes between mill rolls. The intrinsic viscosity of this rubber in toluene at 30° was 5.5, which corresponds to a viscosity average molecular weight of about 1.1×10^6 according to the relation-

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ship established by Carter, Scott and Magat[4]. The "low molecular weight" rubber was obtained by mastication of pale crepe for 20 minutes on a cold mill with close set rolls. Its intrinsic viscosity in toluene at 30° was 1.64, corresponding to a viscosity average molecular weight of about 175,000. Number average molecular weights of the two rubbers presumably were about 500,000 and 100,000, respectively.

Stock solutions in benzene were prepared and stored in darkness. To obtain the proper consistency for the preparation of films, concentrations of about 5 and 10 per cent were chosen for the high and low molecular weight materials, respectively.

Pure decamethylene-dis-methyl azodicarboxylate (referred to as [10–1]) was used exclusively as the cross-linking agent. It was prepared and purified as previously described[1]. In some of the experiments the analogous monofunctional azo compound, ethyl azodicarboxylate (referred to as EAD), was used for the purpose of similarly modifying some of the polymer chain units without introducing cross-linkages. This substance was prepared by the method of Ingold and Weaver[5].

PREPARATION OF VULCANIZATES

The [10–1] disazo compound dissolved in benzene was mixed with the stock solution of rubber in precisely the required proportion and films were cast on glass plates in the manner previously described[2]. It was found advantageous, however, to use a large sheet of plate glass without barriers to confine the viscous solution, the thickness being controlled merely by the rate of drying after pouring the solution onto the plate. The plate was leveled and heated uniformly at 60° for two hours and the vulcanized sheet removed. Thicknesses of different sheets varied from about 3 to 11 mils (thousandths of an inch), but generally were in the vicinity of 5 mils.

In agreement with the indications of the force of retraction measurements[2], heating at this temperature for two hours was adequate for completion of the cross-linking reaction; no significant change in tensile strength was observed when samples were heated for longer periods; in fact, little change in either tensile strength or elongation was noted when the heating period was reduced to one hour.

DETERMINATION OF TENSILE STRENGTH

A diagram of the apparatus employed for the determination of the tensile strength is shown in Figure 1. The method whereby the load is applied by continuous addition of a liquid, in this case water, to a container supported by the sample, is a variation of similar schemes previously applied on various occasions to tensile tests on rubber and on fibers.

Dumbbell specimens of the dimensions shown were cut from the sheets. Their thicknesses were measured at intervals over the constricted portion, using a thickness gauge having a dial divided in 0.1 mil units; interpolations to 0.05 mil appeared to be valid. Samples showing appreciable variation of thickness over the mid section of the dumbbell were discarded. Weights of rectangular strips cut from the mid sections of several dumbbells confirmed the accuracy of the thicknesses determined in the above manner. A pair of ink marks exactly one-half inch apart was placed within the uniform section of the dumbbell.

The dumbbells were fastened between small clamps, each consisting merely of a pair of aluminum plates on the faces of which thin strips of vulcanized

rubber were cemented. The end of the test-specimen was placed between the rubber-covered surfaces of the plates, which were then fastened to one another with a pair of screws running through the plates. The clamp at one end of the sample was anchored in fixed position; the clamp attached to the other end was connected to a fine copper wire which passed over the pulley and to a hook from which a pail could be suspended, as shown in Figure 1. The pulley was pivoted with a ball-bearing of very low friction. In carrying out a determination, the empty pail was attached and gradually lowered until its weight was borne by the sample. Water was then allowed to flow into the pail at a

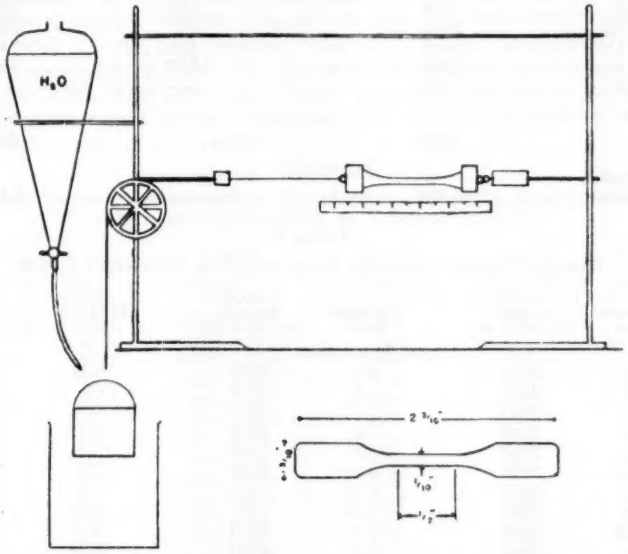

FIG. 1.—Schematic diagram of the apparatus used for tensile strength determinations. The dimensions of the test dumbbells are shown in enlarged scale at the lower right.

constant rate, while a second operator observed the distance between the marks with a ruler. The length at the instant rupture occurred was recorded, and the pail and water it contained were weighed. The tensile strength in pounds per square inch initial cross-section was computed directly. The elongation, expressed as percentage increase in length over the initial length, was obtained in rough approximation only. Tests in which the sample broke at a point appreciably outside the region of uniform section were discarded. Such instances were rare.

RESULTS

Typical results are given in Tables I and II. The former table contains tensile strengths obtained from two sheets separately prepared, using the same proportion of the cross-linking agent, namely 0.30 "equivalent per cent" of [10–1]; in other words, the proportion of the disazo compound employed was sufficient to react with 0.30 per cent of the C_5H_8 units in the rubber (*i.e.*, 0.15 mole of [10–1] per 68 grams of rubber)[6]. Table II gives the results of individual tests on vulcanizates prepared with 1.00 and 3.00 equivalent percent of [10–1].

TABLE I

SAMPLE TENSILE STRENGTH DATA FOR TWO TEST SHEETS OF THE SAME CURE (0.30 EQUIVALENT PER CENT [10–1])

Sheet No. 1		Sheet No. 2	
Thickness of test-peice (mils)	Tensile strength (lb. per sq. in.)	Thickness of test-piece (mils)	Tensile strength (lb. per sq. in.)
4.5	1880	3.85	1920
4.9	1970	4.75	2200
4.5	2140	5.15	2290
2.7	2200	5.35	2310
3.0	2290	5.6	2350
4.35	2340	5.7	2390
5.4	2490	4.8	2410
4.9	2520	5.55	2560
5.25	2630		
Mean	2278	Mean	2304
Av. deviation from mean	±200	Av. deviation from mean	±113

TABLE II

SAMPLE TENSILE STRENGTH DATA FOR TWO DIFFERENT CURES

Thickness (mils)	Tensile strength (lb. per sq. in.)	Thickness (mils)	Tensile strength (lb. per sq. in.)	Thickness (mils)	Tensile strength (lb. per sq. in.
1.00 Equivalent % of [10–1]					
9.4	2520	5.3	3060	5.45	3190
9.4	2560	6.4	3070	11.4	3210
5.9	2600	5.15	3080	5.75	3240
10.3	2710	5.8	3090	5.5	3270
4.6	2740	10.2	3100	7.3	3280
4.35	2820	9.9	3120	5.1	3320
4.5	2960	5.15	3120	5.5	3360
5.0	2990	4.45	3140	5.25	3430
3.85	3000	4.9	3140	5.15	3500
10.6	3000	8.2	3160	5.25	3660
5.75	3060	7.8	3180	7.4	3680

Average deviation from mean: ±200 lb. per sq. in.

Ultimate elongation: 680 ± 15%

3.00 Equivalent % of [10–1]

3.5	1650	3.25	2040	3.2	2120
3.25	1800	5.8	2040	3.5	2250
3.3	1810	2.6	2050	2.6	2260
4.15	1860	7.2	2050	2.8	2270
3.4	1870	3.7	2070	3.3	2290
4.05	1920	3.25	2080	3.4	2330
6.1	1920	3.35	2080		

Average deviation from mean: ±143 lb. per sq. in.

Ultimate elongation: 400 ± 10%

In each of these tables the tensile strengths for a given set are arranged in increasing order. Although the tensile strengths are recorded to the third significant figure, errors of 15 to 50 lb. per sq. in. in the individual determinations are introduced by uncertainties in the sample thicknesses alone.

The results obtained with different sheets prepared with the same proportion of the vulcanizing agent were found to be in good agreement, as is the case for the instance shown in Table I. Hence, results from two or more sheets of the same cure are not differentiated in subsequent tables. Examination of Tables I and II shows that variations in thickness are unimportant. In subsequent tables the thickness of the test-piece has not been recorded. As stated above, however, test sheets usually were close to 7 mils thick.

Principal results of tensile tests on the high molecular-weight rubber are summarized in Table III. In most instances, two or more separate sheets were vulcanized with the same proportion of [10–1] and samples were taken from each of them. Results obtained on high molecular-weight rubber vulcanized with [10–1] and modified with EAD (ethyl azodicarboxylate) are similarly presented in Table IV. Data shown for zero percentages of EAD have been taken from Table III. Table V presents the tensile results for the low molecular weight rubber vulcanized with various proportions of [10–1].

TABLE III

AVERAGE TENSILE STRENGTHS AND ELONGATIONS FOR HIGH MOLECULAR-WEIGHT RUBBER CROSS-LINKED TO VARIOUS EXTENTS

Equiv. % of [10–1]	No. of samples	Average ultimate elongation (%)[a]	Average tensile strength (lb. per sq. in.)	Mean deviation (±lb. per sq. in.)	Root-mean-square deviation, σ (lb. per sq. in.)
0.10	9	1000(±50)	920	204	222
0.20	10	940(±20)	1774	177	194
0.30	17	920(±30)	2288	167	211
0.40	13	850(±20)	2846	184	251
0.50	24	830(±20)	2892	171	209
1.00	33	680(±15)	3102	200	272
1.50	17	570(±25)	2924	200	252
2.00	17	490(±15)	2655	245	288
2.50	11	440(±10)	2353	211	250
3.00	20	400(±10)	2038	143	181
3.20	10	350(±10)	1487	133	171
3.50	14	280(±25)	968	202	242
4.00	16	250(±35)	848	222	265
6.00	13	130(±15)	554	47	59
8.00	13	90(±15)	655	72	79

[a] Figures in parentheses represent approximate mean deviations of the individual elongation measurements.

TABLE IV

TENSILE STRENGTHS OF VULCANIZATES MODIFIED WITH ETHYL AZODICARBOXYLATE (EAD)

Equiv. % of [10–1]	Equiv. % of EAD	No. of samples	Average ultimate elongation (%)[a]	Average tensile strength (lb. per sq. in.)	Mean deviation (±lb. per sq. in.)	Root-mean-square deviation, σ (lb. per sq. in.)
1.00	0	33	680(±15)	3102	200	272
1.00	1.0	12	650(±10)	2994	258	284
1.00	2.2	9	655(±10)	2821	172	177
1.00	4.0	15	650(±10)	2755	160	219
1.00	7.0	10	670(±10)	2404	175	215
0.50	0	24	830(±20)	2892	171	209
0.50	0.50	23	805(±20)	2920	287	324
0.30	0	17	915(±30)	2288	167	211
0.30	0.70	28	895(±15)	2605	173	208
0	1.00	10	1275(±70)	450	76	85

TABLE V

AVERAGE TENSILE STRENGTHS AND ELONGATIONS FOR LOW MOLECULAR-WEIGHT RUBBER CROSS-LINKED TO VARIOUS EXTENTS

Equiv. % of [10–1]	No. of samples	Average ultimate elongation (%)[a]	Average tensile strength (lb. per sq. in.)	Mean deviation (±lb. per sq. in.)	Root-mean-square deviation, σ (lb. per sq. in.)
0.30	16	1080(±35)	909	119	135
0.40	16	970(±25)	1505	173	193
0.50	16	890(±15)	1678	185	222
0.70	14	800(±20)	2195	170	207
1.00	33	690(±20)	2376	236	281
1.30	14	630(±15)	2490	148	174
1.50	11	580(±15)	2563	174	248
1.60	20	590(±15)	2550	266	313
1.80	12	530(±10)	2212	144	170
2.00	7	500(±10)	1803	62	74

[a] Figures in parentheses represent approximate mean deviations of the individual elongation measurements.

Average deviations from the mean and root-mean-square deviations (or standard deviations) σ are given in the last two columns, respectively, of Tables III, IV and V.

Average tensile strengths from Tables III, IV and V are plotted in Figure 2 against the equivalent percentage of the cross-linking agent. Open circles refer to the high molecular weight rubber treated with [10–1] alone, and the solid circles to the vulcanizates prepared from the low molecular-weight rubber. The circles with crosses represent the first set of results given in Table IV; ordinates for these points correspond to the combined percentages of [10–1] and EAD.

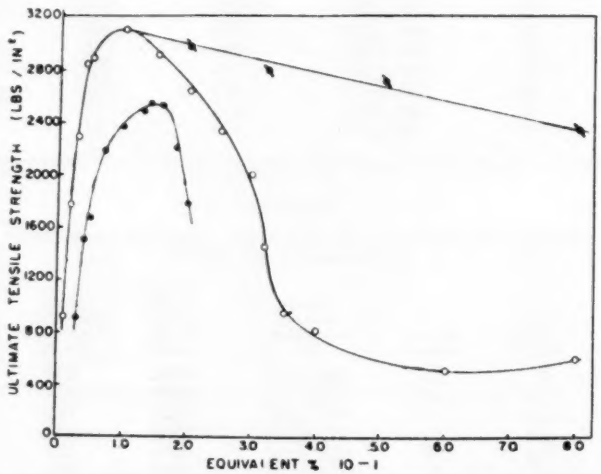

FIG. 2.—Tensile strength (in pounds per square inch) referred to the initial cross-section, plotted against the equivalent percentage ($= \rho \times 100$) of cross-linked units. ○, high molecular-weight rubber (Table III); ⊗, high molecular weight rubber vulcanized with 1.00 equivalent percentage of [10–1] plus varying proportions of EAD, the ordinate representing the combined percentage of azo compounds; ●, low molecular-weight rubber (Table V).

It is immediately evident that marked modification of the rubber by incorporation of ethyl azodicarboxylate depresses the tensile strength very little. In fact, if the EAD adduct is considered to be an inert constituent and the tensile strengths are corrected accordingly to the cross-section of the sample devoid of the EAD modified units, the decrease in the corrected tensile strength is only about 2000 lb. per sq. in. for 7 per cent modification. The marked diminution in tensile strength for higher proportions of [10–1] (alone) must, therefore, be attributed directly to the high degree of cross-linking and not to the secondary effect of modification of the structural units such that they are no longer able to fit into the crystal lattice characteristic of the *cis*-isoprene polymer unit. The ultimate elongation is not affected appreciably by addition of EAD.

Incorporation of EAD in vulcanizates containing less than the optimum proportion (about one equivalent per cent) of [10–1] raises the tensile strength significantly. (See the data in the lower portion of Table IV.) In the total absence of [10–1], one equivalent per cent of EAD yielded a vulcanizate exhibiting measurable tensile strength. Films prepared without addition of either [10–1] or EAD were too weak to be removed from the glass plate on which they were prepared. That the EAD vulcanizate was not cross-linked by primary-valence bonds is clearly shown by the fact that it dissolved readily in solvents such as benzene and chloroform. Evidently the strongly polar hydrazo-dicarboxylate substituents on the polymer chains are capable of interacting sufficiently strongly with one another to enhance the effective degree of cross-linking in tensile measurements. Further evidence that these secondary bonds are readily broken in the presence of solvents is found in the observation that incorporation of EAD does not markedly alter the force of retraction of the vulcanizate at 100 per cent elongation, provided that the stretched sample is equilibrated by temporarily swelling with solvent.

Throughout the tables, and in Figure 2 as well, the tensile strength is referred to the cross-section of the sample before deformation. It is sometimes preferred to express the tensile strength in units referring to the cross-section of the sample at rupture. The latter tensile strength, or tensile product as it has been called, is obtained by multiplying the former tensile strength by the relative length ratio at break. Tensile products for the low and high molecular-weight rubbers vulcanized with [10–1] alone are shown in Figure 3 as functions of the degree of cross-linking. The maxima in the tensile product curves occur at lower elongations. A break in the curve for the high molecular weight rubber is indicated at an equivalent per cent value of 3.0. Although the reality of this discontinuity is not definitely established, it is possible that it may represent the degree of cross-linking above which crystallization does not occur on stretching under the conditions of our experiments (*cf.* seq.).

The dependence of the tensile strength of vulcanized rubber on the degree of cross-linking exhibited in Figures 2 and 3 is in qualitative agreement with the results deduced by Gee[3]. Significant differences are evident, however, on careful comparison. The maxima in Gee's curves for rubbers cured with sulfur and an accelerator (other than those cured using tetramethylthiuram disulfide)[7] occur at degrees of cross-linking in the range from 1.1 to 1.4 equivalent per cent of cross-linked units, which is appreciably beyond the location of the maximum shown in Figure 3 for azo vulcanized rubber of high molecular weight, but only slightly beyond that for the low molecular-weight rubber vulcanizates. Our results indicate a broader range over which the tensile product assumes high

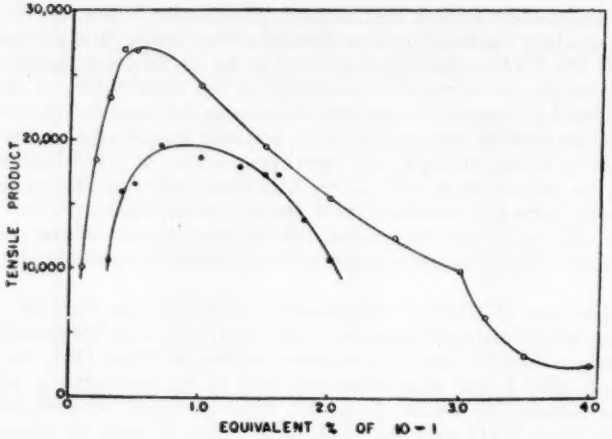

FIG. 3.—Tensile strengths referred to the cross-section at break for the high (○) and low (●) molecular-weight vulcanizates plotted against the degree of cross-linking.

values, and, in particular, the development of appreciable tensile strength sets in at lower degrees of cross-linking. These differences between our results and those of Gee probably arise from inaccuracies in the statistical theory of rubber elasticity on the basis of which Gee's values for the degree of cross-linking were calculated. Observed forces of retraction for low vulcanizates of known degrees of cross-linking are appreciably greater than the values calculated from theory[8]. The fact that our maximum tensile strengths are lower than those obtained by Gee and others may not be significant in view of the vast difference in testing procedures and the difference in dimensions of the test pieces.

DISCUSSION

STATISTICAL ANALYSIS DATA

Mean deviations given in the next to the last columns of Table III, IV and V are similar in magnitude for all vulcanizates excepting those for which the tensile strength is very low. In fact, among all vulcanizates for which the tensile strength exceeds 2000 lb. per sq. in., the variations in the mean deviations recorded in Tables III, IV and V are of the magnitude to be expected for sets of 10 to 20 observations[9], assuming that the same probable error of a single observation applies to all sets. Since this assumption appears to be justified, it is permissible to combine the deviations for individual tests on various vulcanizates and thus obtain a set of deviations sufficiently large for statistical analysis[10]. Accordingly, deviations for all individual tests on samples prepared from the high molecular-weight rubber, using from 0.30 to 3.0 equivalent per cent of [10–1] (Table III), and including also the vulcanizates prepared using EAD in addition to [10–1] (Table IV)[11], were combined. The resulting set is comprised of 262 deviations, each of which represents the difference between the observed tensile strength for an individual test and the average for all tests on the same cure. Owing to statistical errors in the values for these averages, the combined set of deviations may be expected to cover a slightly narrower range than would have been obtained for an equal number of indi-

vidual tests on the same vulcanizate. The error from this source should be small since the number of tests at each cure was large enough to reduce the probable error of the mean for that cure to a fairly low figure. The mean deviation for the combined set of 262 deviations was 201 lb. per sq. in., the standard deviation was 248 lb. per sq. in. The number of tests for which the deviation falls within each 100 lb. per sq. in. interval is plotted in Figure 4 against the location of the interval (*e.g.*, the number of deviations for the interval −300 to −200 lb. per sq. in. is represented by a point located at −250 along the abscissa). The curve drawn in the figure represents the Gaussian error function for which the standard deviation is that observed for the combined set (*i.e.*, 248 lb. per sq. in.). Close agreement between the observed points and the error function is evident[12].

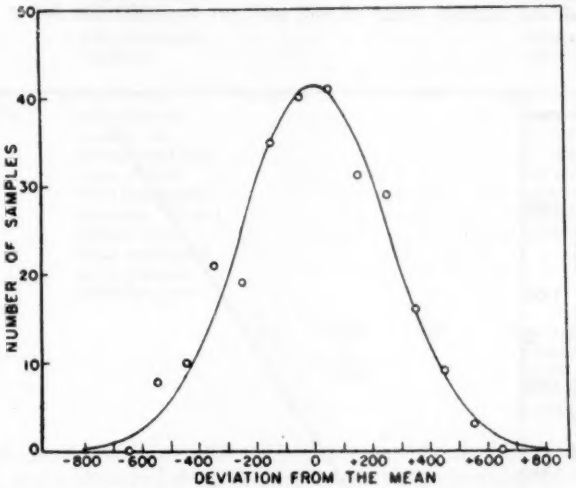

FIG. 4.—Distribution of combined deviations from the mean for all tests at 14 different cures. Each point represents the number of deviations falling within a 100 lb. per sq. in. interval.

A somewhat better comparison of the same data with the Gaussian function is afforded by the probability paper plot shown in Figure 5. The plot is linear within experimental error throughout most of the range, with some suggestion of small departures at the extremities (see also Figure 4). Thus, there is a slightly greater incidence of very large negative deviations than the Gaussian function would predict, and the incidence of very large positive deviations appears to be too small. However, omission of two or three of the observations in which extreme deviations were observed would eliminate this evidence for asymmetry. On the whole the deviations from the mean are remarkably well represented by the Gaussian function, the apparent skew character at the extremities being indecisive.

In Table VI results of other investigations[13] on the distribution of deviations in tensile strength measurements are summarized. In general the distribution is approximately Gaussian, although previous results do not yield as close agreement with the Gaussian function as has been found to be the case for the tests reported here. An excessive number of very low values occurs and a

slight deficiency for large positive deviations seems indicated. The presence of the former may readily arise from unobserved flaws in a few of the samples. On the other hand, Braendle and Wiegand[14], using a vulcanizate which presumably contained a small proportion of carbon black, found a markedly skew distribution which cannot be approximated by the Gaussian function.

The view has often been advanced that rupture of the tensile test specimen is initiated invariably at spurious flaws in the test-piece, and that the result of a given test merely records the weakest link in the series of flaws (of whatever origin) along the length of the specimen. The true tensile strength, according to this hypothesis, may never actually be realized, owing to the intercession of the flaws. The highest observation would therefore represent the closest approach to the true tensile strength. Proceeding from this concept, it has been common practice to average three measurements which are within 10 per cent of the highest value of the set[15], or to otherwise favor the higher observations[16].

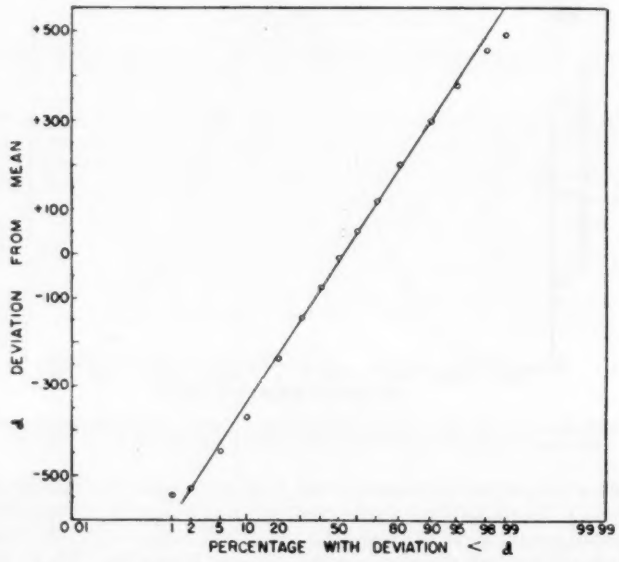

FIG. 5.—Probability paper plot of the combined deviations from the mean.

A statistical analysis of the weakest link hypothesis has recently been published by Epstein[17], who shows that a Gaussian (symmetrical) distribution of strength measurements scarcely can be expected on this basis. Furthermore, the average tensile strength should depend on the dimensions of the test-piece. Observed results are at variance with these predictions. Not only is the distribution of deviations accurately Gaussian under favorable conditions, as noted above, but the standard deviations appear to be remarkably uniform for a variety of conditions, including the fifty-fold difference in cross-sectional area of our test-pieces, compared with those used in the other investigations. The weakest link hypothesis quite clearly is inapplicable to vulcanized rubber.

TABLE VI

SUMMARY OF THE RESULTS OF STATISTICAL ANALYSES OF TENSILE STRENGTH DETERMINATIONS

Investigators	Material and method	No. of tests	Average tensile strength (lb. per sq. in.)	Standard deviation (lb. per sq. in.)	Distribution of deviations from mean
Braendle and Wiegand[14]	Samples cut from a commercial inner tube; Scott rubber tester used	95	2637	170	Skew distribution with excess of low values and deficiency of high ones
Fric[37]	Rubber-sulfur (7.5%) vulcanizates tested with Schopper machine	731	2230	ca. 180	Approximately Gaussian except for frequent occurrence of very low values
Davies and Horrobin[19]	205 different vulcanizates, usually six specimens from each, tested with Schopper machine. Individual deviations combined as in present investigation	ca. 1000		162	Approximately Gaussian except for small excesses of values far from the mean, especially at very large negative deviations
Present investigation		262	2000 to 3000	248	Close agreement with Gaussian curve, although slight asymmetry is indicated at extremities

These facts, in conjunction with the perhaps equally significant approximate constancy of the standard deviation for a wide range in vulcanizate structure (see Tables III and V), should be given foremost consideration in any attempt to formulate an acceptable structural theory of tenacity in such materials.

Entirely apart from theoretical considerations pertaining to the nature of the phenomenon of rupture under stress, the fact that the deviations from the mean assume the Gaussian form invalidates arbitrary selection of the test measurements to be averaged. Rejection of values far from the mean, including very high as well as very low values, may be justified, however[18]. For example, Davies and Horrobin[19] suggested that from a set of five or more observations any which are outside the range $+2\,\sigma$ may be rejected. Bias resulting from conventional arbitrary selection of the test values has been discussed by Buist and Davies[16].

The probable error for a single observation when the Gaussian function is obeyed being $0.675\,\sigma$, the probable error applying to the bulk of our measurements (samples of low tensile strength excepted) is 167 lb. per sq. in. The probable error in the mean of n observations is given by $0.675\,\sigma/n^{1/2}$. Ten or more tests were made for each cure, hence the probable errors in the average tensile strengths given in Tables III, IV and V are about 80 lb. per sq. in. or less. This degree of precision is confirmed by the consistency of the results plotted in Figure 2.

TENSILE STRENGTH IN RELATION TO NETWORK STRUCTURE

The critical dependence of tensile strength on crystallization of stretched rubberlike materials has often been emphasized. Recently, correlations of tensile strength with the network structure of the vulcanizate have been attempted through consideration of the factors affecting crystallization on stretching[20]. The relationship of the tensile strength of Butyl rubber to the molecular weight before cross-linking (primary molecular weight) has been accounted for semi-quantitatively from this point of view[21]. It was shown that the tensile strength at fixed degree of cross-linking increases approximately linearly with the fraction of the structure which is permanently oriented by stretching. This fraction, representing the portion of the polymer occurring in chains bounded at both ends by cross-linkages, is given by:

$$w_A = 1 - 2M_c/(M + M_c) \tag{1}$$

where M is the primary molecular weight (the number average should be used), and M_c is the weight per mole of cross-linked units.

$$M_c = 68/\rho$$

where ρ is the fraction of the isoprene units involved in cross-linkages ($100\,\rho$ equals the equivalent percentage of 10–1). Equation 1 may be replaced by:

$$w_A = (\rho\bar{x}_n - 1)/(\rho\bar{x}_n + 1) \tag{2}$$

$$\cong 1 - 2/\rho\bar{x}_n \tag{2'}$$

where $\bar{x}_n$ represents the number average degree of polymerization of the primary molecules.

The investigation on Butyl rubber[21] was largely confined to the influence of primary molecular weight on tensile strength, with limited results bearing on the effect of the degree of cross-linking. The bulk of the results were obtained at a fixed degree of cross-linking corresponding to a ρ value of 0.16×10^{-2}. In view of the two chain atoms in the isobutylene unit compared with four for the isoprene unit in rubber, a figure twice this one should perhaps be employed in drawing comparisons with the present results. Even with this alteration, such a comparison would place the principal set of results on Butyl rubber in the region well to the left of the maximum in the plot of tensile strength *vs.* the degree of cross-linking shown for the high molecular-weight rubber in Figure 2. Tensile strengths of Butyl polymers at about twice this degree of cross-linking (ρ about 0.25×10^{-2}) were lower, however. Thus, it is indicated that the corresponding maximum in the curve for Butyl rubber occurs at a very low degree of cross-linking.

In contrast to the previously reported study of vulcanized Butyl rubber, the present results are largely confined to the influence of the degree of cross-linking on tensile strength, with only meager results bearing on the role of primary molecular weight. For degrees of cross-linking up to the regions of the maxima, the tensile strength curves shown in Figure 2 for the low and the high molecular-weight rubbers are related to one another in the approximate manner to be expected on the assumption that the tensile strength is primarily dependent on the weight fraction w_A of active network as given by Equations (1) and (2). To attain the same tensile strength, the low molecular-weight rubber must be cross-linked to about three times the extent required for the high molecular-weight rubber over this range. Thus, if the primary molecular

weight of the latter is assumed to be three times that of the former, roughly the same tensile strength is obtained for the two rubbers when M_c/M; hence w_A of Equations (1) and (2) has the same value for each. The viscosity average molecular weights of the two rubbers (see below) indicated a probable ratio for the primary molecular weights of about five. The difference between the effective molecular weights for the two rubbers may have been narrowed somewhat by the occurrence of chain scission to a small extent during preparation of the vulcanizates. While this possible complication precludes quantitative verification of the direct dependence of the tensile strength on the fraction w_A of the network structure which is permanently oriented by stretching, the results indicate that this factor is of dominant importance throughout the region of low degrees of cross-linking preceding the maximum in the curve. The precipitous rise in the tensile strength with degree of cross-linking in this range provides further confirmation of this conclusion, since w_A increases rapidly with ρ for small values of the latter.

The occurrence of a maximum in the tensile strength *vs.* degree of cross-linking curve and the subsequent decrease in tensile strength for higher extents of vulcanization seem to be related to the diminished ultimate orientation which is attained as the degree of cross-linking is increased. It is well known that crystallization sets in at a lower elongation the higher the degree of cross-linking. A recent theoretical treatment[22] of crystallization in stretched rubber indicates that the critical elongation for incipient crystallization (at equilibrium at a given temperature) should vary approximately as the inverse square root of the degree of cross-linking; *i.e.*, directly as the square root of the average length of a chain between cross-linkages. In effect, then, the higher the degree of cross-linking, the lower the elongation at which some of the chains become sufficiently oriented to undergo crystallization. Such crystallization increases the effective degree of cross-linking[22] of the chains involved and consequently the degree of crystallinity increases more rapidly with further elongation of the sample. The ultimate degree of crystallinity is rapidly attained, the retractive force rises steeply and rupture occurs at an elongation which may be related, qualitatively at least, to the elongation for incipient crystallization. Therefore, as the degree of cross-linking increases, both the elongation for incipient crystallization and the ultimate elongation decrease in roughly parallel fashion.

The relationship between the orientation of the network structure and the elongation may be approached from consideration of the action of an elongation on the set of chain displacement vectors, each of which leads from one cross-linkage to the next along the same chain. On stretching the sample, this set of vectors is distorted from a spherical to an ellipsoidal array. If the sample is stretched to the relative length α, it is readily shown that the fraction of the vectors elongated by the factor κ or greater is given by:

$$f_\kappa = 1 - [(\kappa^2\alpha - 1)/(\alpha^3 - 1)]^{1/2} \tag{3}$$

which function only gradually approaches unity with increase in α for a given value of $\kappa \geqq 1$. It is to be noted that f_κ is independent of the degree of cross-linking. Only those chains which are sufficiently oriented and elongated (the processes of orientation and elongation being mutually related) are potentially capable of participating in the formation of crystallites. The fraction of the chains meeting this requirement clearly depends sharply on α. Hence, an increase in the degree of cross-linking lowers the elongation at which some of the structure may crystallize, but the fraction which is sufficiently oriented to

participate in the formation of crystallites, even at the breaking elongation, is diminished[13]. According to the hypothesis that tensile strength is related directly to the fraction of the structure oriented sufficiently to allow it to participate in the formation of crystallites, the tensile strength should exhibit a corresponding decrease as the degree of cross-linking is increased, in accordance with observation at degrees of cross-linking beyond the maximum in the curve.

The increase in the tensile strength which accompanies rise in testing temperature up to about 100° C according to certain results[24] cited by Gee[3] also may be explained on the basis of the above considerations. In accordance with the conclusion reached by Gee in this connection, an increase in temperature shifts the onset of crystallization to a higher elongation where a larger fraction of the chains are sufficiently oriented to undergo crystallization. Ultimate elongations were observed to increase with the temperature also[24].

At higher degrees of cross-linking (*i.e.*, beyond $\rho \times 100 = 3.0$ for the high molecular-weight rubber) rupture presumably occurs before the onset of crystallization. In these higher vulcanizates the force of retraction rises rapidly with elongation in accordance with the theory of rubber elasticity (in the absence of crystallization) and may exceed the inherent strength of the material before it is reinforced by crystallization. This idea, mentioned previously by one of the authors[21], has been developed in considerable detail by Gee[3], who suggests it as the major factor responsible for the decline in the tensile strength beyond the optimum degree of cross-linking. In our opinion, however, it assumes importance only under conditions such that the observed tensile strength is very low, *e.g.*, at degrees of cross-linking well beyond the maximum in the tensile strength curve, for very low primary molecular weights, or at temperatures (or dilutions) such that the tensile strength is only a few hundred pounds per square inch. The steep decline occurring near $\rho \times 100 = 3.0$ in the curve shown in Figure 2, and the corresponding intimation of a break in the curve of Figure 3, may be indicative of the degree of cross-linking beyond which crystallization on stretching vanishes.

EFFECTS OF FOREIGN UNITS ON TENSILE STRENGTH

The results obtained with the ethyl azodicarboxylate modified vulcanizates (Table IV; also shown in Figure 2) demonstrate that modification of up to 7 per cent of the isoprene units with a substituent which is three times the size of the isoprene unit reduces the tensile strength relatively little. Previous emphasis[20] on the influence of small percentages of foreign units on the crystallinity and, hence, on the tensile strength appears to be unwarranted. Some other explanation is required for the decrease in tensile strength of vulcanizates from Butyl rubber having 1.0 or more mole per cent of diolefin as compared with vulcanizates from Butyl polymers having half this proportion of the unsaturated unit[21]. Likewise, it now appears highly unlikely that the tensile strength of rubber vulcanized with sulfur and an accelerator is materially affected either by cyclization or by noncross-linking reactions with sulfur, as has been suggested by Gee[3].

According to recent investigations into the nature of crystallization in polymers and copolymers[25], introduction of foreign units at random along the polymer chain will lower the temperature for incipient crystallization, or "melting point", but a large depression requires a correspondingly large proportion of the foreign unit; the effect of the foreign units in the polymer chain

resembles that of an impurity on the melting point of a monomeric substance. The degree of crystallinity at a given temperature below the melting point is suppressed to a somewhat greater extent. The most decisive effect of an occasional foreign unit which is incapable of entering the crystal lattice is the limitation of the lengths of the crystallites which may be formed. In the light of these considerations, the observed behavior of the EAD modified vulcanizates suggests that crystallites of great length are unnecessary for the realization of high tensile strength, and, furthermore, that the actual degree of crystallinity is not of direct importance. The crystallites presumably enhance the tensile strength by cementing adjacent chains together laterally at various regions along their lengths. Approximately the same tensile strength apparently may be achieved through the participation of each chain of the copolymer, *i.e.*, partially modified polymer, in a number of shorter crystalline regions as through the presence of a fewer number of long crystallites in the unmodified polymer. According to the present results this remains true despite the much smaller degree of crystallinity to be expected in the copolymer. Hence, it is the fraction of the chains of the network structure which are induced to enter into crystallite formation at one or more regions along their lengths which is important, rather than the actual degree of crystallinity. At sufficiently high degrees of modification of the chain units, the tensile strength may fall to a low value owing principally to depression of the melting point to the extent that little or no crystallization occurs on stretching.

The above conclusions are corroborated by the rather small effect of random copolymerization on the tensile strength of high melting oriented polyamide and polyester fibers[25]. Although the tensile strength generally decreases somewhat with increasing proportions of the comonomer, the capacity for exhibition of high tensile strengths are by no means destroyed even in 1 : 1 random copolymers. The residual elongation of the fully drafted fibers is appreciably increased by copolymerization, however.

OVERCURE AND AGING IN RUBBER VULCANIZED WITH SULFUR AND ACCELERATORS

When the curing period is prolonged in the conventional vulcanization of rubber, or if the vulcanizate is heat-aged, the tensile strength passes through a maximum, beyond which it decreases with further heating. In the light of the above results, this decrease in tensile strength, commonly referred to as overcure, cannot be attributed to modification of the chain units as suggested by Gee[3]. The continued formation of cross-linkages or the occurrence of chain scission (or both) would, however, explain the observed decrease.

The modulus, or force of retraction, of many compounds similarly passes through a maximum and then declines with further heating. According to the theory of rubber elasticity, the equilibrium force of retraction[26] should be proportional to:

$$(1 - 2M/M_c) \cong (1 - 2/\rho\bar{x}_n)$$

The so-called phenomenon of reversion of the cure may, therefore, be due either to rupture of previously formed cross-linkages (a decrease in ρ), or to chain scission which causes M, and $\bar{x}_n$, to decrease. Simultaneous decreases in both tensile strength and modulus of highly cross-linked vulcanizates, *i.e.*, beyond the maximum in Figure 2, indicate unambiguously, therefore, that chain scission takes place. Other changes, such as a decrease or increase in

the degree of cross-linking, may of course occur simultaneously. It is to be noted that the elastic modulus and the tensile strength are affected differently by variation in $\bar{x}_n$, this being evident from the above expression and the discussion given in the preceding sections. Hence characterization of the rubber by its force of retraction alone is inadequate.

Gee has shown[3] that two vulcanizates prepared from different compounds, but cured for times such that they exhibit the same force of retraction at a given elongation, generally exhibit markedly different tensile strengths. The lack of a direct correlation between tensile strength and modulus for rubber specimens vulcanized with different accelerators seems to be general, and it again points to the occurrence of differing degrees of chain scission.

While quantitative results are as yet limited, it is now clearly indicated that the apparently irrational dependence of various physical properties of vulcanized rubber on the complexities of the recipe and time of cure can be resolved logically in terms of two extremely simple structure variables: the degree of cross-linking and the primary molecular weight. A third variable, the degree of modification of the chain units, now appears to be of trivial importance, at least insofar as tensile strength is concerned.

SYNOPSIS

The tensile strengths of natural-rubber samples quantitatively cross-linked with decamethylene dis-methyl azodicarboxylate have been determined. The proportion of the azo vulcanizing agent was varied 80-fold, the fraction ρ of cross-linked units in the products ranging from 0.10×10^{-2} to 8.0×10^{-2}. In spite of the small dimensions of the test-specimen (cross-section 0.10 in. by about 0.005 in.), the average error for a single observation is similar to that obtained in conventional testing procedures applied to specimens vulcanized with sulfur and accelerators. Deviations from the mean for 262 tests on 15 different cures are well represented by a Gaussian error function; a slight intimation of skewness is evident only at the extremities of the distribution of deviations. These results are incompatible with the commonly held view that rupture of the sample takes place at the weakest link in the series of flaws inevitably occurring along the specimen. It would appear that the ability to withstand tensile stress (applied in a specified manner) is an inherent characteristic of the bulk material. The rapid increase in tensile strength with the degree of cross-linking ρ for small values of this quantity is consistent with the conclusion, previously reached in the investigation of the physical properties of Butyl rubber[21], that the tensile strength is directly related to the fraction of the structure which is permanently oriented by stretching. At higher degrees of cross-linking (at $\rho \times 100 = 1.0$ to 1.5, depending on the molecular weight of the rubber), the tensile strength passes through a maximum and then declines steadily to very low values for higher ρ values. This adverse effect of higher degrees of cross-linking is believed to result from the diminished elongation at which crystallization sets in; hence, the smaller fraction of the network elements sufficiently oriented to participate in crystallite formation. Modification of up to 7 per cent of the isoprene units of the rubber with the monofunctional compound, ethyl azodicarboxylate, depresses the tensile strength of the disazo vulcanized rubber relatively little. Evidently, the limited extent to which these modified (or copolymer) chains may enter into crystallization is adequate to bring about high tensile strength. Lack of direct correlation between modulus and tensile strength for rubbers vulcanized with

various sulfur-accelerator combinations can be explained only by assuming that conventional vulcanization processes are accompanied to varying degrees by chain-scission reactions. When vulcanized rubber is overcured, or heat-aged, chain scission becomes excessive.

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[6] The "equivalent percentages" used throughout this paper correspond to $\rho \times 100$ of the earlier paper (Flory, Rabjohn and Shaffer, *J. Polymer Sci.* **4**, 225 (1949); RUBBER CHEM. TECH., preceding paper in this issue).

[7] Compare the curves in Figure 3 of this paper with curves C, D and E of Figure 5 of Gee (*J. Polymer Sci.* **2**, 451 (1947)).

[8] Flory, *Ind. Eng. Chem.* **38**, 417 (1946); Flory, Rabjohn and Shaffer, *J. Polymer Sci.* **4**, 225 (1949); RUBBER CHEM. TECH., preceding paper in this issue.

[9] Margenau and Murphy, "The Mathematics of Physics and Chemistry", New York, **1943**, p. 496.

[10] The deviations from the means for measurements on 205 different rubber vulcanizates were combined in this manner by Davies and Horrobin (*Trans. Inst. Rubber Ind.* **12**, 85 (1936)). In most cases six tests were performed on each sample, but some were represented by fewer tests. With such small numbers of individual tests on each specimen, the combined set of deviations is not accurately representative of the actual deviations from the true mean values.

[11] Mean deviations for the thirteen tests of a vulcanizate not reported in Tables III and IV were also included in the combined set of 262 deviations. This sample was prepared with 0.8 equivalent per cent of [10–1] and 0.2 equivalent per cent of EAD. Tests of the low molecular-weight rubber vulcanizates, for which the mean tensile strength exceeded about 2000 lbs. per sq. in., might also have been included, but were not.

[12] In calculating the curve in Figure 4, the modulus of precision h in the Gaussian error function: $y = (h/\pi^{\frac{1}{2}}) \exp(-h^2d^2)$, where y is the frequency of occurrence of deviations per unit interval at deviation d, has been assigned the value: $h = (1/\sigma\sqrt{2})$, where σ is the observed standard deviation, *i.e.*, 248 lb. per sq. in.

[13] Fric, *Chimie et Industrie*, Special No., Apr. **1928**, p. 541, Braendle and Wiegand, *Ind. Eng. Chem. Anal. Ed.* **1**, 113 (1929); Davies and Horrobin, *Trans. Inst. Rubber Ind.* **12**, 85 (1936).

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RELATIONSHIP BETWEEN GOUGH-JOULE COEFFICIENTS AND MODULI OF VULCANIZED RUBBERS *

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INTRODUCTION

The first reference to the increase in temperature of rubber on stretching was by Gough[1], but this was apparently unnoticed until Joule[2] rediscovered the phenomenon. Joule's experiments showed a decrease in temperature with increase in elongation up to about 2 per cent and an increase in temperature with increase in elongation beyond this point. He recognized also that the principles of thermodynamics require that a rubber strip elongated by a constant load must become shorter when heated.

Subsequent investigations have been made on the change in length of a rubber strip with a change in temperature at constant load[3] and on the change in force with change in temperature at constant elongation[4]. The use of three concepts to designate the same phenomenon indicates an awareness of interrelationships among them, but this relationship has not been explicitly stated. The latter two concepts lend themselves most readily to quantitative measurements, and will be referred to as the Gough-Joule effects at constant stress and at constant strain, respectively.

Investigations of the Gough-Joule effect in vulcanized rubber have been very productive of knowledge concerning the physical structure of rubber. The use of rubberlike materials as support members has also emphasized the practical importance of the effect. In such cases it is important to know the interrelationship of the Gough-Joule coefficients and moduli.

The greatest experimental difficulty experienced by investigators in the field has been the attainment of thermodynamic equilibrium, and various methods have been used to minimize creep and plastic flow during experiments. Williams[3] obtained stress-strain curves with extreme rapidity and was able to show the increase in modulus of stretched rubber with increased temperature. Gerke[4] obtained equilibrium deformations by means of either horizontal or vertical vibrations in stretched samples. Meyer and Ferri[5] held the desired elongation at the highest temperature of test until increase in length became negligible. Meyer and van der Wyk[6] obtained torsional deformations alternately 5° C higher and 5° C lower than the test temperature until plastic deformation tended to disappear. In the present work it was found that a specimen which had been kept under a given shear stress for 16 hours at 35° C was essentially in stress-strain equilibrium (within the time required for the experiment) at temperatures below 35° C. This method of conditioning was, therefore, used in all of the experimental work described below. The advan-

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tages of conditioning at temperatures above the test temperatures is apparent from a consideration of the fact that, in the absence of chemical changes or crystallization, the same equilibrium strain-temperature curve is eventually reached at any temperature at which the test-specimen is elastic. Temperatures much above 35° C could not be used because of the accelerated rate of chemical changes.

Most of the early work on the Gough-Joule effect was done in tension[7]. The disadvantages of this type of deformation have recently been pointed out by Meyer and van der Wyk[6]. They show that the apparent change of sign of the effect at 0.10 strain is due to volume change and, hence, is eliminated when shear deformation is used.

Another time-dependent factor besides creep and plastic flow often influences the attainment of thermodynamic equilibrium. This is crystallization. A second important advantage of a shear type of specimen for work of this nature is that shear does not appear to induce crystallization to the same extent as does equivalent tension or compression. It has been shown in this laboratory, for example, that a particular Hevea stock did not crystallize during a period of six hours at −20° C under a shear strain of 1.07. The same stock, by its low recovery rate, showed definite evidence of crystallization after 6 hours storage at 40 per cent compression at −20° C.

MATHEMATICAL DEVELOPMENT

Suppose a specimen of rubber is acted upon by a stress σ which produces a strain γ at absolute temperature T. Let C be the thermal capacity of the specimen, H its intrinsic energy or enthalpy. Assuming no significant difference between C_σ and C_γ a single symbol may be used for either.

CASE I. CONSTANT STRAIN

Let T and σ be changed by small amounts with γ held constant, then the heat received by the strip:

$$dQ = CdT + C(\partial T/\partial\sigma)d\sigma \tag{1}$$

The work done on the strip is $\gamma d\sigma$, hence:

$$dH = dQ + \gamma d\sigma = CdT + C(\partial T/\partial\sigma)d\sigma + \gamma(\partial\sigma/\partial T)dT$$

or

$$dH = [C + \gamma(\partial\sigma/\partial T)]dT + C(\partial T/\partial\sigma)d\sigma. \tag{2}$$

The change in entropy is:

$$dS = \frac{dQ}{T} = \frac{C}{T}dT + \frac{C}{T}\left(\frac{\partial T}{\partial\sigma}\right)d\sigma \tag{3}$$

Since dS and dH are perfect differentials the Euler equations may be applied to Equations (2) and (3) to yield:

$$\frac{\partial C}{\partial\sigma} + \left(\frac{\partial\gamma}{\partial\sigma}\right)\left(\frac{\partial\sigma}{\partial T}\right) = 0 \tag{4}$$

and

$$\frac{\partial C}{\partial\sigma} = \frac{\partial C}{\partial T}\frac{\partial T}{\partial\sigma} \tag{5}$$

Eliminating $\partial C/\partial\sigma$ between (4) and (5) and solving for $\partial\sigma/\partial T$ we have:

$$\frac{\partial C}{\partial T}\frac{\partial T}{\partial \sigma} = -\frac{\partial \gamma}{\partial \sigma}\frac{\partial \sigma}{\partial T} \tag{6}$$

The quantity $(\partial\sigma/\partial T)_\gamma$ will be called the Gough-Joule coefficient at constant strain.

CASE II. CONSTANT STRESS

Following a similar development for the case of constant stress we may show that:

$$\frac{\partial C}{\partial T}\frac{\partial T}{\partial \gamma} = -\frac{\partial \sigma}{\partial \gamma}\frac{\partial \gamma}{\partial T} \tag{7}$$

The quantity $(\partial\gamma/\partial T)_\sigma$ will be called the Gough-Joule coefficient at constant stress. From Equations (6) and (7) we obtain:

$$\left(\frac{\partial\sigma/\partial T}{\partial\gamma/\partial T}\right)^2 = \left(\frac{\partial\sigma}{\partial\gamma}\right)^2$$

or

$$\frac{\partial\sigma/\partial T}{\partial\gamma/\partial T} = -\frac{\partial\sigma}{\partial\gamma} \tag{8}$$

In the case of a rubberlike material $\partial\gamma/\partial T$ is negative, and all other terms in Equation (8) are positive. Hence only the negative sign is applicable to the right-hand member of the equation[8].

The second member of Equation (8) is the slope of the stress-strain curve at the point (σ, γ), and may be termed the *tangent modulus* of the stock at this point. It has thus been shown that the ratio of the Gough-Joule coefficient at constant strain to that at constant stress is equal to the tangent modulus.

If it is initially assumed that there exists some function of σ, γ, and T and no other thermodynamic variable such that:

$$f(\sigma, \gamma, T) = 0 \tag{9}$$

then Equation (8) may be derived much more simply. By a well known mathematical theorem it follows from Equation (9) that:

$$\left(\frac{\partial\sigma}{\partial\gamma}\right)\left(\frac{\partial\gamma}{\partial T}\right)\left(\frac{\partial T}{\partial\sigma}\right) = -1 \tag{10}$$

which is equivalent to Equation (8).

It will be shown later that over a wide temperature range the magnitude of the Gough-Joule coefficient at constant stress is directly proportional to the stress (Figure 5), and that the Gough-Joule coefficient at constant strain is directly proportional to the strain (Figure 6). The quotients $(\partial\sigma/\partial T)_\gamma/\gamma$ and $(\partial\gamma/\partial T)\sigma/\sigma$ are thus constant over considerable portions of the stress-temperature and strain-temperature curves. From Equation (8) we obtain:

$$\frac{(\partial\sigma/\partial T)_\gamma \cdot (1/\gamma)}{(\partial\gamma/\partial T)_\sigma \cdot (1/\sigma)} = -\left(\frac{\partial\sigma}{\partial\gamma}\right)_T \cdot \frac{\sigma}{\gamma} \tag{11}$$

The member on the right of Equation (11) is the product of the tangent modulus and the *secant modulus*, where secant modulus is used to denote the quotient of the total stress to the strain produced by that stress.

The following experimental work was performed to test the validity of Equations (8) and (11) as applied to a variety of compounds. Both the type of polymer and the pigmentation were varied.

DESCRIPTION OF APPARATUS

The apparatus used was basically one developed by H. Leaderman and one of the authors (G. L. Hall), for use in the study of creep and recovery. The diagram in Figure 1 shows that the apparatus consists essentially of a means of applying a constant shear stress or a constant shear strain to a double sandwich type of specimen, and of observing the deformation of the specimen as test conditions are varied. The side plates of the test-specimen are firmly gripped in slots in a jig. An extension rod clamped to the central steel member of the specimen passes through the housing; the dial gauge spindle rides on this extension rod. The dial gauge used has graduations of 0.0001 inch.

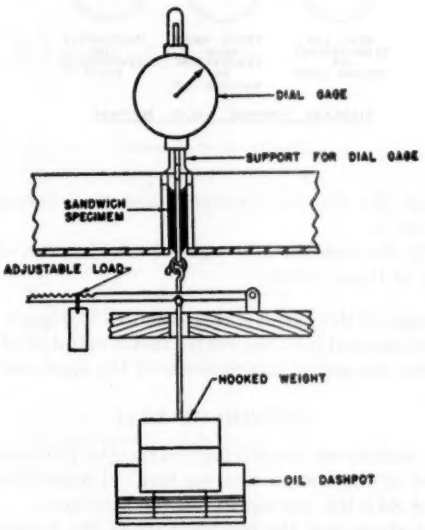

FIG. 1.—Diagram of apparatus.

The load is applied by lowering a hooked weight so that it engages with a ring attached to the central member of the sandwich. The basic hooked weight is provided with an oil dashpot at its lower end to damp out horizontal oscillations.

The housing or air thermostat in which the jig is placed is shown in Figure 2. Air is blown into the thermostat by means of a centrifugal blower over heater coils, some of which are controlled by a bimetallic thermoregulator through a lock-in type relay, and some of which are uncontrolled. According to the setting of the gate valve shown in Figure 2, the air leaving the thermostat may either

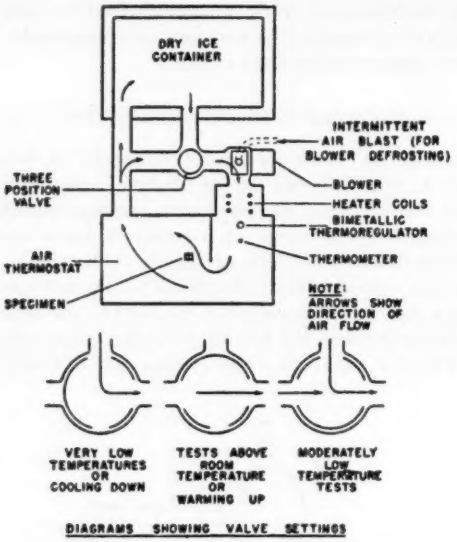

FIG. 2.—Air thermostat.

(1) pass through the dry ice container, and then through the gate valve to the blower, or
(2) pass directly through the gate valve to the blower, or
(3) follow both of these paths.

The three settings of the gate valve are shown in Figure 2.

A thermocouple inserted into the center metal member of the test-specimen was used to measure the actual temperature of the specimen at all times.

METHOD OF TEST

Each specimen tested was conditioned overnight (16 hours) at 35° C under the load to be used in the constant stress test. Unless otherwise stated, this load was 100 lbs. or 35.6 lbs. per sq. in. on the specimen.

In the constant stress test the temperature of the housing was lowered at such a rate that a constant temperature differential of 15° C was maintained between the housing and the specimen. Dial gauge readings were obtained at 5° C intervals down to the temperature at which the strain-temperature curve departed from linearity. The temperature was then raised to 35° C at such a rate that a 15° C temperature differential was maintained between the housing and the specimen and again making dial gauge readings at 5° C intervals. The slopes of the resulting strain-temperature curves are almost identical, and are only slightly displaced from one another. The temperature gradient within the specimen when the temperature of the housing is being raised or lowered thus appears to be relatively unimportant. Figure 3 shows typical data obtained in this manner. The compound used in this case was Hevea compound *B* (Table I). The average slope of the straight line portions of the two curves is taken as the Gough-Joule coefficient at constant stress.

TABLE I

COMPOUNDING FORMULAS

Pigment cure	Hevea *A* 35′/288° F	Hevea *B* 50′/280° F	Hevea *C* 35′/288° F	Butyl GR-I 30′/312° F	Neoprene GR-M 60′/280° F	GR-S 60′/280° F	Butaprene (medium acrylonitrile) 60′/280° F
Polymer	100	100	100	100	100	100	100
Sulfur	3	3	3	1.5	—	2	2
Zinc oxide	3	5	3	4	5	5	5
Stearic acid	0.5	3	3.5	—	0.5	—	1
Channel black	—	15	50	30	20	20	45
SRF black	—	15	—	—	20	15	—
Mercaptobenzothiazole	1	—	1	1	—	—	—
PBNA	1	1	1	—	—	—	2
Pine tar	—	—	3	—	—	—	—
808 accelerator	—	—	—	—	—	0.25	—
Dibutyl sebacate	—	—	—	—	—	—	20
Medium process oil	—	2.5	—	—	—	—	—
Paraffin	—	—	—	2	—	—	—
Light calcined magnesia	—	—	—	4	4	—	—
Methyl tuads	—	—	—	1	—	—	—
Benzothiazoyl disulfide	—	0.75	—	—	1	—	1
Neozone-D	—	—	—	—	2	—	—
Light process oil	—	—	—	—	15	—	—
Petrolatum	—	—	—	—	2	—	—
Paraflux	—	—	—	—	—	5	—
Turgum-S	—	—	—	—	—	8	—
Santocure	—	—	—	—	—	1.25	—

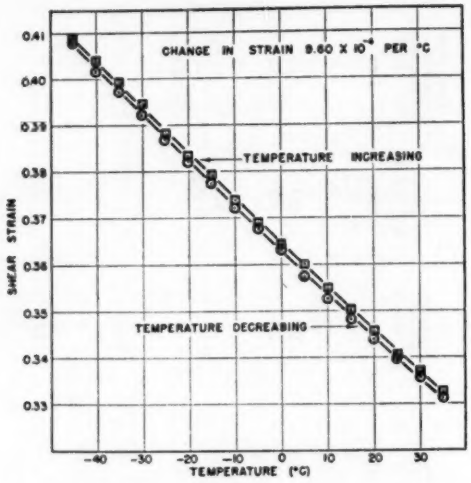

FIG. 3.—Gough-Joule effect under constant stress of 35.6 lbs. per sq. in., Hevea compound *B*.

In the constant-strain tests, the same specimen as previously tested under constant stress was first brought to a temperature corresponding to the center of the linear portion of the strain-temperature curve. The resulting strain was then maintained constant by varying the position of the load on the lever arm shown in Figure 1. The temperature was altered in the manner previously described and the load recorded at 5° C intervals. The data shown in Figure 4 on the Hevea compound *B* is typical of stress-temperature curves obtained in this manner. Duplication of the original stress after traversing the temperature cycle shows the system to have been in equilibrium during the process.

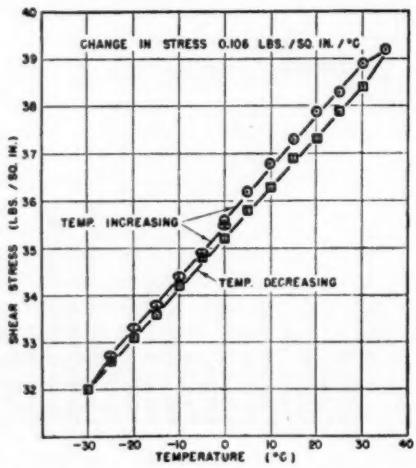

FIG. 4.—Gough-Joule effect under constant strain of 0.365, Hevea compound *B*.

The tangent modulus was obtained at a temperature corresponding to the middle point of the linear portion of the strain-temperature curve. A 10-lb. additional load (3.56 lbs. per sq. in.) was added to the specimen and the resulting deflection noted after 30 minutes. This 10 lbs. and another 10 lbs. were then removed from the specimen and the recovery was noted after 30 minutes. The tangent modulus was taken as the mean of the moduli obtained by addition and subtraction of the 10-lb. loads. In the case of the Hevea Compound *B* the modulus obtained by addition of the 10-lb. load was 108.5 lbs. per sq. in. and that obtained on removal of the load was 114.0 lbs. per sq. in.

Table I shows the formulas and cures of the compounds employed in these tests. Five commonly known polymers are represented. Three degrees of black content of Hevea compounds are included to show the effect, if any, of these compounding changes on the validity of Equations (8) and (11).

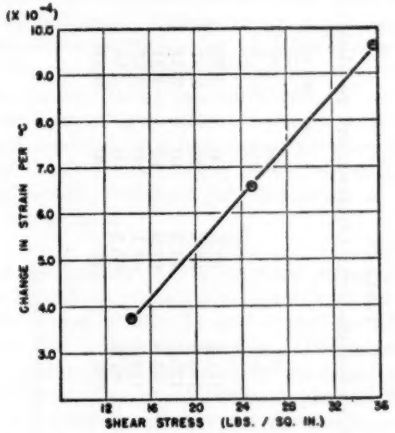

FIG. 5.—Effect of degree of stress on Gough-Joule effect at constant stress, Hevea compound *B*.

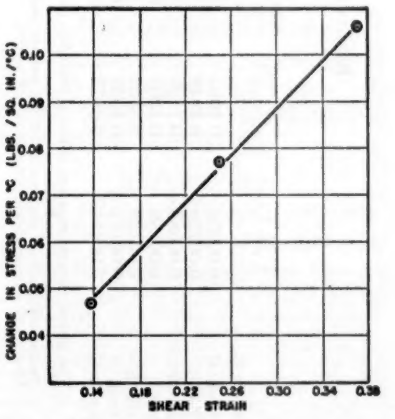

FIG. 6.—Effect of degree of strain on Gough-Joule effect at constant strain, Hevea compound *B*.

TABLE II

RELATIONSHIPS OF GOUGH-JOULE COEFFICIENTS TO MODULI

Compound	$\left(\frac{\partial\gamma}{\partial T}\right)_\sigma$ (° C^{-1})	$\left(\frac{\partial\sigma}{\partial T}\right)_\gamma$ (lbs./in.^{2}/° C)	$\frac{(\partial\sigma/\partial T)_\gamma}{(\partial\gamma/\partial T)_\sigma}$[a] (lbs./in.^{2})	$\frac{\Delta\sigma}{\Delta\gamma}$[b] (lbs./in.^{2})	$\frac{\sigma}{\gamma}$ (lbs./in.^{2})	Ref. temp. ° C	$\frac{(\partial\gamma/\partial T)_\sigma}{\sigma}$ ($\times 10^{-5}$) (in.^{2}/lb./° C)	$\frac{(\partial\sigma/\partial T)_\gamma}{\gamma}$ (lbs./in.^{2}/° C)	$\frac{(\partial\sigma/\partial T)_\gamma}{\gamma} \Big/ \frac{(\partial\gamma/\partial T)_\sigma}{\sigma}$[c] (lbs./in.^{2})^2	$\frac{\Delta\sigma}{\Delta\gamma}\cdot\frac{\sigma}{\gamma}$[d] (lbs./in.^{2})^2
Hevea *B*	0.00096	0.1060	110.4	111.2	97.5	0	2.70	0.293	10,850	10,710
GR-S	0.00139	0.1642	118.1	112.4	87.8	20	3.91	0.398	10,180	9,860
Butaprene	0.000835	0.1120	134.4	135.2	74.2	10	2.34	0.237	10,130	10,030
Butyl	0.00150	0.1300	86.7	85.8	61.9	15	4.21	0.226	5,370	5,310
Neoprene	0.00120	0.1350	112.5	114.1	64.1	0	3.37	0.243	7.210	7,310
Hevea *A*	0.00167	0.1053	63.1	67.0	65.5	0	4.58	0.194	4,240	4,390
Hevea *C*	0.000148	0.0872	588	596	319	0	0.416	0.781	188,000	190,000

[a] Theoretical tangent modulus obtained from Eq. (8).
[b] Measured tangent modulus.
[c] Theoretical value of the product of the tangent and secant moduli from Eq. (11).
[d] Product of measured tangent and secant moduli.

RESULTS

In every case investigated the Gough-Joule coefficient at constant stress was directly proportional to the stress and that at constant strain was directly proportional to the strain. A typical illustration of this behavior is shown in Figures 5 and 6 for the Hevea low black stock. Within rather wide limits, then, the quotient $(\partial\gamma/\partial T)_\sigma/\sigma$ and $(\partial\sigma/\partial T)_\gamma/\gamma$ are independent of the stress and strain at which they were obtained. These values are thus characteristic of the particular compound and do not depend on test conditions.

Table II shows the relevant data obtained on the compounds given in Table I. The close agreement of columns 4 and 5 shows that Equation (8) is true experimentally for the compounds studied. In the same manner, the agreement of the last two columns verifies Equation (11) experimentally.

In Table II:

$(\partial\gamma/\partial T)_\sigma$ = Gough-Joule coefficient at constant stress for 100 lb. (35.6 lbs. per sq. in.) load. Change in strain per degree C.

$(\partial\sigma/\partial T)_\gamma$ = Gough-Joule coefficient at constant strain (that produced by 35.6 lbs. per sq. in. load at reference temperature). Change in stress (in lbs. per sq. in.) per degree C.

$\Delta\sigma/\Delta\gamma$ = Tangent modulus at reference temperature (in lbs. per sq. in.).

σ/γ = Secant modulus at reference temperature (in lbs. per sq. in.).

$(\partial\gamma/\partial T)_\sigma/\sigma$ = Gough-Joule coefficient per unit stress at constant stress.

$(\partial\sigma/\partial T)_\gamma/\gamma$ = Gough-Joule coefficient per unit strain at constant strain (in lbs. per sq. in.).

SUMMARY

The Gough-Joule coefficients (1) at constant stress and (2) at constant strain are defined and methods of measurement of each on vulcanized rubbers are given. It is shown mathematically and experimentally that the ratio of (3) to (4) is equal to the "tangent" modulus. The quotient of the Gough-Joule coefficient at constant stress divided by the stress and the quotient of the Gough-Joule coefficient at constant strain divided by the strain are shown to be constants which are independent of the stress-strain-temperature conditions. Experimental data are given for stocks based on Hevea, GR-S, Neoprene-GN, Butyl Rubber, and Butaprene.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of discussions on the Gough-Joule effect with J. W. Ballard and W. E. Loue. The continued interest of E. W. Ford is much appreciated as is the permission of The Firestone Tire and Rubber Company to publish these results.

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[8] Gee, *Quart. Rev. Chem. Soc.* **1**, 265 (1947). It should be observed that the Gough-Joule coefficient at constant stress can be calculated from the tangent modulus at a given stress and temperature. It has been pointed by Gee (*loc. cit.*) that $(\partial H/\partial\gamma)_{T,\sigma} = 0$ for shear deformations. Making use of this relation, it can be readily shown that $(\partial\gamma/\partial T)_\sigma = \sigma/T \cdot 1/(\partial\sigma/\partial\gamma)$. Values of $(\partial\gamma/\partial T)\sigma$ calculated from this formula are not, however, in close agreement with observed coefficients given in Table 2. The difference between the observed and calculated values is as high as 30 per cent in some cases.

TIME AND STRESS EFFECTS IN THE BEHAVIOR OF RUBBER AT LOW TEMPERATURE *

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INTRODUCTION

The behavior of rubber at low temperature is complicated, the overall performance representing the combined effects of several entirely different phenomena. These have been studied rather thoroughly by many investigators, and the general principles will be illustrated here only by way of review.

Generally near room temperature the modulus of elasticity increases with increasing temperature, in agreement with the usual kinetic theory of molecular motion[1]. This is illustrated in Figure 1 which shows the dependence of dynamic

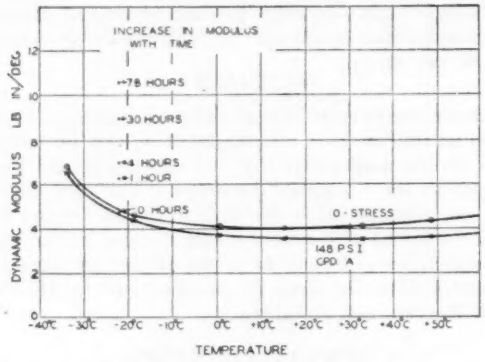

FIG. 1.—Effect of temperature on the dynamic modulus of rubber.

modulus on temperature for a lightly loaded carbon black stock under two conditions, with no shear stress and with considerable shear stress. Above 15° C, although the change is very small, the slope is positive. Below room temperature the curve deviates from the predictions of kinetic theory, and the rubber becomes progressively stiffer until, in the region of −55° to −65° C, the modulus is very high, in the neighborhood of 10^6 lb. per sq. in. This is the region of the second order transition[2], and apparently the flexibility of the individual chains has decreased and the attraction between neighboring chains has increased to such an extent that the material no longer has rubberlike properties. Just above the second order transition temperature the rubber has leatherlike properties and shows high hysteresis[3].

The manner in which the modulus curve deviates from the kinetic theory predictions around room temperature is affected greatly by several factors[4].

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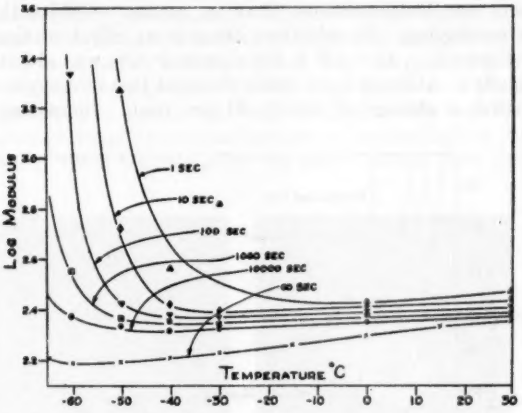

FIG. 2.—Effect of rate of deformation on the modulus of rubber.

The effect of rate of deformation is illustrated by the results in Figure 2 taken from a previous paper by Greene and Loughborough[5]. For very slow rates of deformation the behavior follows the kinetic theory predictions to lower temperature, and the change from rubberlike to rigid material is relatively sharp. The nature of this change is influenced greatly by loading pigments, particularly carbon black. As shown by Figure 3, also taken from the paper

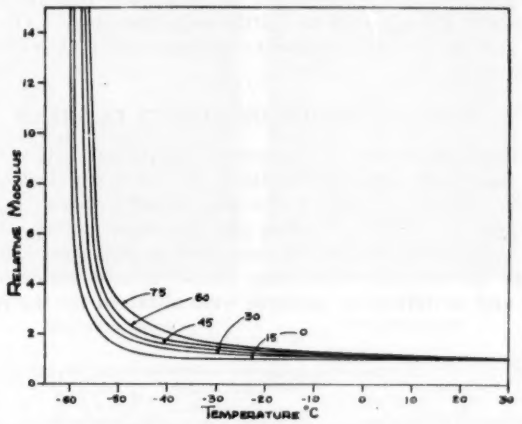

FIG. 3.—Effect of carbon black on the modulus of rubber.

referred to above, these loading pigments have the same general effect as increasing the speed of deformation.

All rubberlike polymers act essentially alike, but there is considerable difference in the second order transition temperature, and the stiffness on approaching this temperature[2], as shown[5] in Figure 4. For the materials shown, Neoprene-FR stiffens at the highest temperature; Butyl, GR-S, natural rubber, and polybutadiene stiffen at progressively lower temperatures.

The effects are instantaneous, that is, rubber exhibits these properties immediately on cooling. In addition, there is an effect of time of exposure, as shown in Figure 1. At −22° C the dynamic rate was about 4.8 lb.-in. per degree, originally. After an hour under stress at this temperature the rate had increased to 6.3, a change of nearly 30 per cent. Increasing the exposure

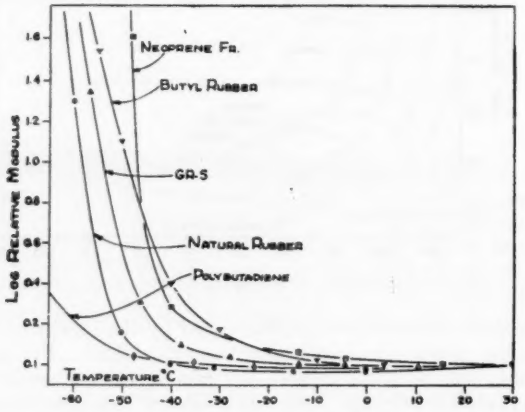

Fig. 4.—Comparison of modulus of various polymers at low temperature.

changed the rate to 7.1 at 4 hours, 9 at 30 hours, and 10.5 at 78 hours, a total increase of nearly 120 per cent in a little over three days. Obviously, this is the effect of another kind of mechanism superimposed on the effects of the two discussed above.

CRYSTALLIZATION OF RUBBER IN SHEAR

One obvious explanation of this increase in stiffness is that the rubber has crystallized, and x-ray diffraction patterns for rubber under shear show that to be the case. The sample was a thin slice, about $\frac{1}{4}$-inch thick, of the sample shown in Figure 5. Using a holding jig, the central shaft was turned with respect to the outer shell and held in that position with the x-ray beam perpendicular to the flat surface. The shear stress varies considerably throughout this sample, and so diffraction patterns were obtained for the region near the

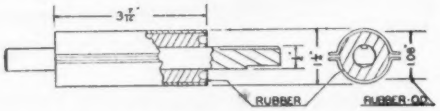

Fig. 5.—Diagram of sample.

shell and near the shaft. Figures 6A and B show the patterns for these two regions at room temperature. There is very little evidence of crystallization—none at all in the low shear region, and perhaps just a slight indication in the high shear region. After 48 hours at −22° C, the patterns shown in C and D were obtained. The pattern for the high shear region shows rather sharp arcs

indicating considerable crystallization. The low shear region is not quite as sharp, but again there is no doubt that considerable crystallization has taken place. This was accepted as sufficient proof that the gradual increase in stiffness shown in Figure 1 was actually due to crystallization of the rubber.

The crystallization of rubber has been studied rather extensively[6]. Generally, this has emphasized the crystallization on stretching[7] or on exposure to low temperature[8]. On a few occasions the slow changes that take place after

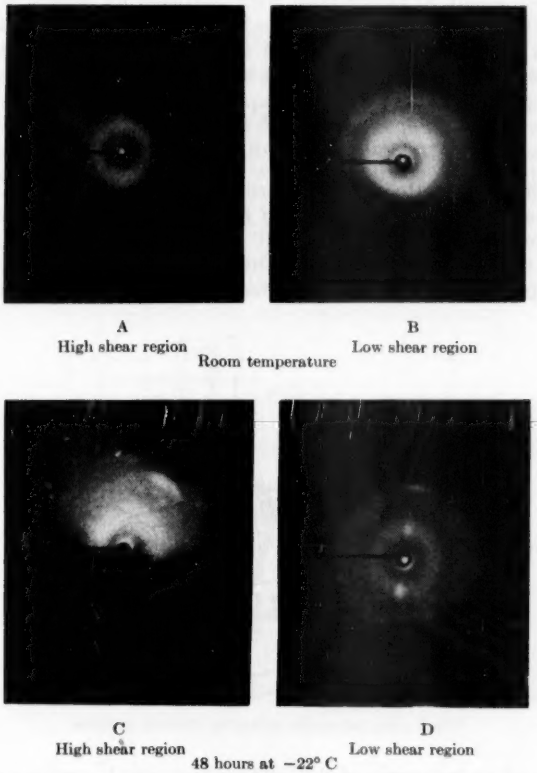

FIG. 6.—*x*-Ray diffraction patterns of ¼-in. thick slices of sample shown in Figure 5.

stretching have been studied[9], but generally the experiments have been arranged to emphasize either instantaneous crystallization or the relatively slow crystallization which takes place at low temperature under no stress. In the present experiments the conditions were just right to emphasize the crystallization taking place in a stressed sample on further exposure to low temperature.

Further comparisons of the elasticity measurements and diffraction patterns indicated that the dynamic modulus test provided a much more sensitive measure of the changes that were taking place. Fairly large changes in modulus occur without corresponding detectable changes in diffraction patterns.

Accordingly, the modulus test was used for studying these changes, and the effects were generally interpreted as resulting from crystallization, or at least incipient crystallization.

EXPERIMENTAL METHOD

The sample used in all cases was that shown in Figure 5 and the test equipment, that shown in Figure 7. These have been described previously[10]. The sample is mounted horizontally with the shaft held rigidly. Attached to the shell is an arm about 30 inches long, with provision for adding weights up to about 26 pounds at each end. When the loading arm is displaced and released, the resulting free vibration provides a convenient measure of the dynamic elastic properties. The dynamic spring rate is given by:

$$k = \frac{4\pi^2 I f^2}{g}$$

where k is the spring rate, I the moment of inertia of the vibrating system, g the acceleration due to gravity, and f the frequency of free vibration. For the loads generally used, $k = 33.6 \times 10^{-4} f^2$, where k is in lb.-in. per degree, and f is in vibrations per minute. The frequency, in the neighborhood of 1 vibration per second, is determined from an autographic chart made by a

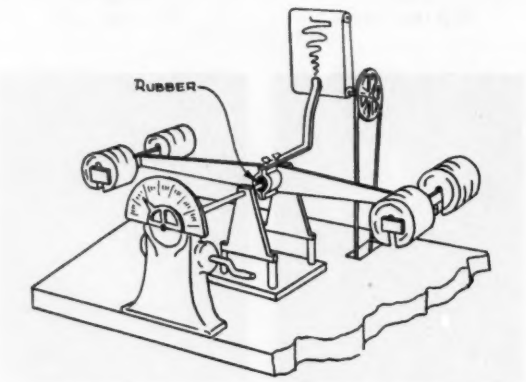

FIG. 7.—Equipment for measuring dynamic modulus.

stylus, fastened to the center of the loading arm, which scribes a record of the motion of the arm on moving wax paper driven by a synchronous motor. One end of the shaft is held by the driven shaft of a gear reducer; with balanced or unbalanced weights on either end of the loading arm, this gear reducer provides a convenient way of winding up the sample to keep the loading arm horizontal. For example, in many of the experiments, the load on one end was 19 pounds and on the other end 7 pounds, giving a steady torque of 180 lb.-in. or a stress at the shaft of 148 lb. per sq. in. The vertical load on the sample undoubtedly has some slight effect on the results, but the major effect results from the wind-up. This wind-up is measured on a circular scale.

In all cases the sample was cooled to the desired temperature under no stress. Time effects were measured from the instant torque was applied.

The shear stress throughout the sample varies inversely with the square of the radius, and with this sample the range is about 4/1 from the inside layer near the shaft to the outside layer near the shell. For this reason it is difficult to express the results as a dynamic modulus of the rubber. Moreover, the dynamic modulus is not uniform throughout the sample. Crystallization very likely proceeds much more rapidly near the shaft. Accordingly, the results are left in the less definite form of a dynamic rate for the particular test sample. This is essentially an average modulus for all the rubber in the sample but this average is determined mainly by the rubber near the shaft.

RESULTS

The results in Figure 1 were obtained for a sample of Compound A, a lightly loaded carbon black stock. The same results are plotted in Figure 8 to show more directly the effect of time and stress. The striking effect here is the rapid rate of change of modulus at 148 lb. per sq. in. At zero stress there is no apparent change. Bekkedahl and Wood[11] found for unstressed samples that

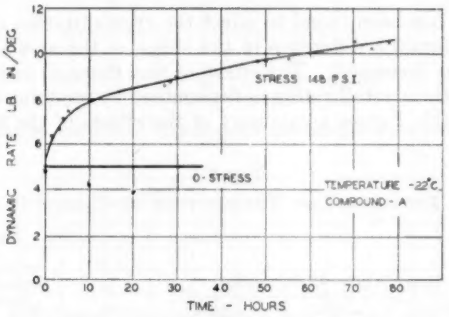

FIG. 8.—Change in dynamic modulus of rubber with time and stress.

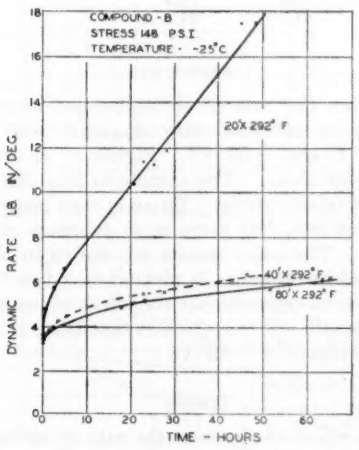

FIG. 9.—Effect of cure on the rate of stiffening.

it required about 200 days for an appreciable amount of crystallization to take place at this temperature. At 148 lb. per sq. in. the effect seems to be at least 50 times faster.

STATE OF VULCANIZATION

Figure 9 shows the effect of time of cure for Compound B, a pure-gum natural rubber stock. Increasing the number of bonds between chains should decrease the tendency to crystallize, and this is the effect found. There is a great deal of difference between the 20-min. and the 40-min. cures but little change near the optimum as shown by the 80-min. cure.

Since the degree of vulcanization has a large effect on the manner in which the rubber crystallizes, it is difficult to study some of the factors which influence the rate and amount of crystallization. There is always some uncertainty as to whether other effects are not overbalanced by effects of cure. In the examples which follow, it seems certain that the other effects are much greater than those that might be expected from variations in cure.

CARBON BLACK

Carbon black has been found to affect the crystallization of rubber. Gehman and Field[12] found a difference in the shape of the arcs as the amount of channel black was increased. The effect of fine thermal and easy processing channel black on the crystallization as determined by modulus changes is shown in Figure 10. Table I gives a summary of the effects of the blacks.

TABLE I

SUMMARY OF EFFECT OF LOW TEMPERATURE ON CARBON BLACK STOCKS

	Dynamic rate—lb.-in. per deg.			Per cent increase of dynamic rate	
Compound	Room temp.	−25° C 0 hr.	−25° C 24 hrs.	Instantaneous R. T. to −25° C	After 24 hrs. at −25° C
B	2.2	3.2	5.1	45	59
C	3.7	5.5	10.7	49	95
D	6.8	10.9	21.5	60	97

TEMPERATURE

For unstressed rubber the rate of crystallization depends greatly on the temperature. There is an optimum rate at about −25° C, with very slow crystallization at +10° C and −50° C[6]. Figure 11 shows the effect of temperature for rubber under shear. The sample in this case was Compound E, a lightly loaded natural rubber stock. There is very large increase in the rate as the temperature is lowered, but there is no evidence of any optimum temperature in this region. The same results are shown in Figure 12, where the dynamic rate at the end of 30 hours is plotted as a function of temperature. Here an attempt is made to separate out the effect of instantaneous stiffening. This effect is relatively small, and it is obvious that there is a very rapid increase in crystallization in the region of −30° C.

STRESS

Figure 13 shows the effect of stress on the rate of stiffening for the sample. These results are also plotted in Figure 14, again separating out the instan-

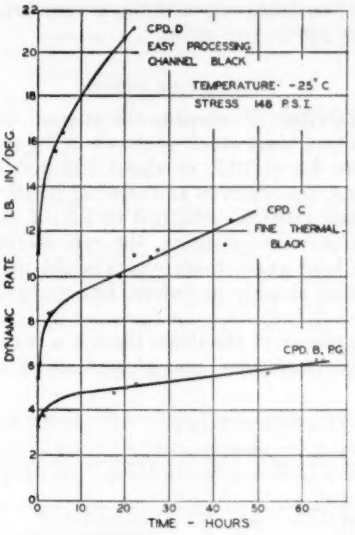

FIG. 10.—Effect of carbon black loading on modulus changes at low temperature.

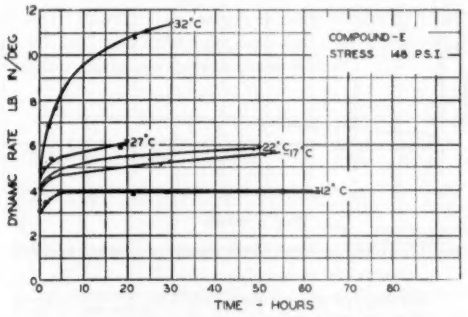

FIG. 11.—Effect of temperature on change in dynamic modulus.

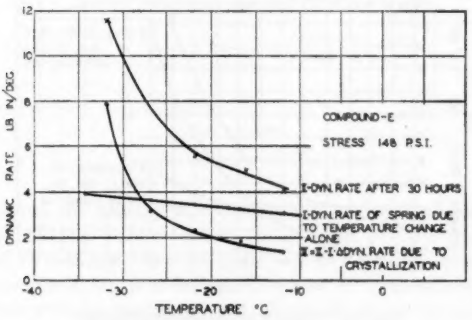
COMPOUND-E
STRESS 148 P.S.I.
I-DYN. RATE AFTER 30 HOURS
I-DYN. RATE OF SPRING DUE TO TEMPERATURE CHANGE ALONE
II=I-I'-ΔDYN. RATE DUE TO CRYSTALLIZATION
DYNAMIC RATE LB IN/DEG
TEMPERATURE °C

FIG. 12.—Effect of temperature on crystallization.

taneous effects. The remaining curve shows a very great effect of increasing stress, especially above 200 lb. per sq. in.

RELEASE OF STRESS

Figure 15 shows the effect of releasing the stress. This sample was of the same lightly loaded carbon black stock as shown in Figures 1 and 8. After the stiffness increased from 4.8 to 10.5, or about 120 per cent, over a period of about 78 hours, the load was removed and after 32 hours, still at a temperature of $-24°$ C, the dynamic rate had returned to 5.3, or only about 10 per cent above the original value. On reloading, the rate increased about as before, and on removing the load again there was a slight decrease. On reloading again, the rate increased roughly as before, but presumably somewhat more slowly.

Apparently during release of the stress there is a tendency to break up any alignment of the rubber molecules, and at zero stress, of course, the rate of

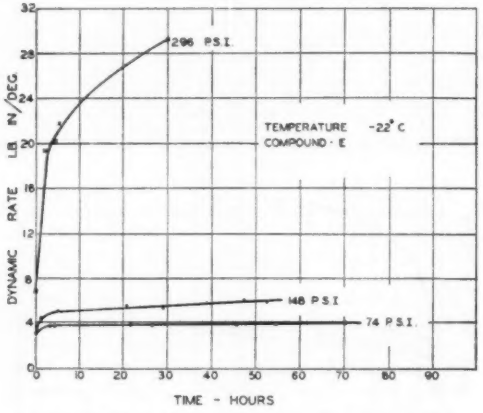

FIG. 13.—Effect of stress on the change in dynamic modulus.

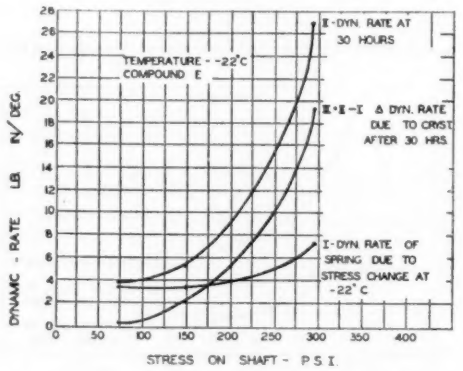

FIG. 14.—Effect of stress on crystallization.

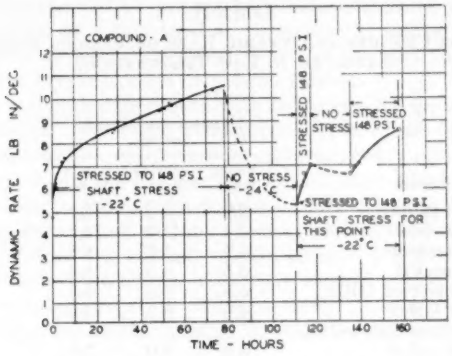

FIG. 15.—Effect of repeated stressing on modulus changes.

crystallization is very slow. On reapplying stress the process either starts from the beginning or, if some residual alignment remains, as for example at 134 hours, proceeds from that point about parallel to the previous curve.

COMPARISON OF POLYMERS

It is commonly known that some polymers, such as polybutadiene and in particular copolymers such as Neoprene-FR and GR-S, do not crystallize nearly as readily as natural rubber. In fact it is only recently that x-ray evidence of such crystallization has been obtained, and for this it has been necessary to cool the sample to low temperature before stretching[13].

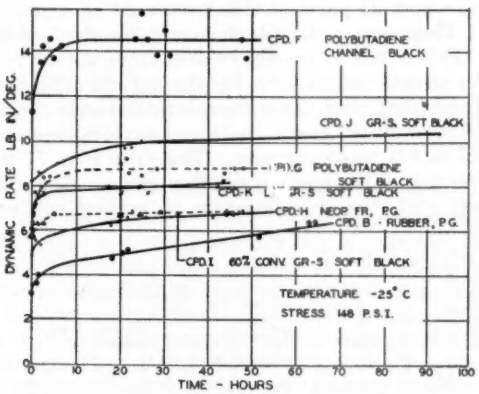
CPD. F POLYBUTADIENE CHANNEL BLACK
CPD. J GR-S, SOFT BLACK
CPD. G POLYBUTADIENE SOFT BLACK
CPD. K GR-S SOFT BLACK
CPD. H NEOP FR, P.G.
CPD. B - RUBBER, P.G.
CPD. I 60% CONV. GR-S SOFT BLACK
TEMPERATURE -25° C
STRESS 148 P.S.I.
DYNAMIC RATE LB IN/DEG
TIME - HOURS

FIG. 16.—Comparison of polymers.

Figure 16 shows the change in dynamic rates of several polymers compared with the rate of natural rubber stock, Compound B. Polybutadiene, both in a soft black and in a channel-black recipe, shows a typical crystallization curve. Neoprene-FR seems to show a definite increase in dynamic rate. Three types of GR-S polymers were investigated. They all show crystallization; an un-

TABLE II

SUMMARY OF CHANGES IN DYNAMIC RATE OF VARIOUS POLYMERS ON EXPOSURE TO LOW TEMPERATURE

Compound	Polymer	Dynamic rate in ln.-in. per deg.			Per cent increase of dynamic rate	
		Room temp.	−25° C 0 hr.	−25° C 24 hrs.	Instantaneous R. T. to −25° C	After 24 hrs. at −25° C
B	Natural rubber	2.2	3.2	5.1	45	59
F	Polybutadiene	7.4	11.3	14.4	53	27
G	Polybutadiene	4.5	5.7	8.8	27	54
H	Neoprene-FR	3.5	4.9	6.6	40	35
I	60% converted GR-S	5.5	5.8	6.6	5.5	14
J	Regular GR-S	4.0	8.1	9.9	102	22
K	Low-temperature polymerized GR-S	3.5	6.0	7.9	71	32

modified 60 per cent conversion GR-S least, the standard GR-S slightly more, and a low-temperature polymerized GR-S most. The results are summarized in Table II. In all cases the effects of crystallization are appreciable, but less than shown by natural rubber stocks. Moreover, all of these synthetic polymers show a much greater tendency to level off at some definite value.

MIXTURES OF POLYMERS

Figures 17 and 18 show the effect of mixing polymers. It might be expected that, on mixing a polymer that does not crystallize readily with natural rubber, the amount of stiffening would be decreased merely by dilution. However, with the matrix predominately natural rubber this effect should be small. Figure 17 shows the crystallization curves for a natural rubber stock, a GR-S stock, and one in which 25 parts of GR-S replaced an equivalent amount of natural rubber. There was a definite tendency for the GR-S to reduce the crystallization. This is not so readily evident from the curves. During the first 24 hours the increase in modulus for the natural rubber stock was from 4.8 to 8.5, or 77 per cent, and the corresponding change for the GR-S stock was from 8.1 to 9.9, or 22 per cent. With the mixture, however, the increase was only from 5.7 to 9.0, or 58 per cent. This drop from 77 to 58 per cent is more than is expected on the basis of dilution alone. Apparently, the GR-S actually interferes with the crystallization of natural rubber. Such inter-

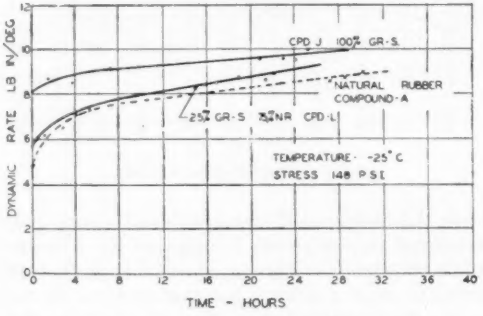

FIG. 17.—Stiffening of mixtures of natural rubber and GR-S.

ference would be expected on mixing two materials which have different repeating periodicities, or which tend to crystallize in unlike patterns. x-Ray diffraction patterns of similar mixtures bear out the idea that GR-S actually interferes with the crystallization of natural rubber.

In Figure 18 a similar experiment with Neoprene-FR gave different results. In this case a natural rubber and a Neoprene-FR stock are compared with one made from a combination of 75 parts of natural rubber and 25 parts of Neoprene-FR. Since Neoprene-FR contains an inhibitor which acts as an accelerator of vulcanization for natural rubber in this case, the Neoprene-FR was extracted with acetone before mixing. Here apparently the mixture crystallizes just as rapidly as does the natural rubber stock. The reason is not exactly clear, but probably it is a question of thoroughness of mixing. Natural rubber and GR-S appear to be compatible and form an intimate mixture on a molecular scale. If the Neoprene exists in small discrete particles, then the only inter-

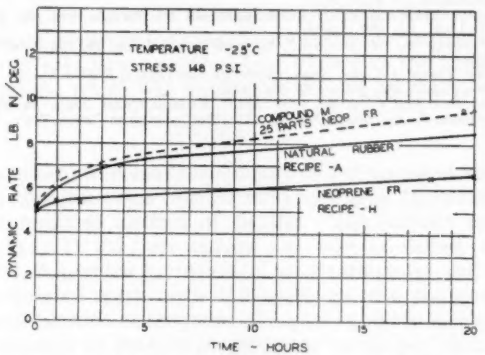

FIG. 18.—Stiffening of mixtures of natural rubber and Neoprene-FR.

ference to crystallization would be at the interfaces, which would affect only a small part of the volume of the natural rubber. This would account for the effects shown in Figure 18.

SUMMARY

The stiffening of rubberlike materials at low temperature involves several different phenomena, sometimes with their effects superimposed. One of these is crystallization. This is a rate process which is generally very fast at high stresses and very slow at zero stress. In these experiments at temperatures near $-25°$ C and under a shear stress of about 148 lb. per sq. in. the dynamic modulus of the rubber increased at a rate convenient to study. Correlation with x-ray data showed that crystallization was very likely responsible for the increase in stiffness. The rate of change of stiffness increased rapidly with increase in applied stress, and there was no optimum rate at $-25°$ C, as has been found for unstressed rubber. The degree of vulcanization influenced the rate of change, tighter cures giving smaller changes. Neoprene-FR, GR-S, and polybutadiene, which ordinarily show little evidence of crystallization, showed very definite, but small increases in stiffness. Mixing GR-S with natural rubber seems to limit the crystallization of the natural rubber rather effectively, but apparently Neoprene-FR does not mix intimately enough with natural rubber to affect the crystallization of the latter appreciably.

ACKNOWLEDGMENT

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FLOW PHENOMENA IN RUBBER SAMPLES *

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In an earlier effort to explain some of the properties of balloons, numerous measurements of rubber samples were carried out[1], and the surprising fact was revealed that balloons may rupture at low temperatures as a result of cold flow. This is, however, in accord with observations of the flight of balloons, particularly their almost constant rate of ascent. Since this flow proceeds parallel with a hardening of the material, it is of added interest in connection with problems of structure, which in the case of rubber involve various peculiarities[2]. The phenomenon of cold flow was, therefore, chosen as the subject of a more extended investigation, which was finished at the end of 1944.

APPARATUS

To study by mechanical means the elongation and tensile strength of rubber samples, a simple apparatus was constructed (see Figure 1b) which in principle followed the conventional method of testing. The cut-out test-specimens, shown in Figure 1a in 1 : 2.5 their natural size, were stretched to the point of rupture in about 1–2 minutes by means of an electromotor and spring dynamometer. An imprinted mark made it possible to read the elongation at all times, so that the elongation at the point of rupture and the entire course of the stress-strain curve could be read by stopping the motor periodically.

Since flow is only slight at room temperature and since in these experiments the results were only comparative, the method used for measuring the stress-strain curves at room temperature was considered satisfactory[3].

At low temperatures, at which flow becomes of more importance, the method had to be changed somewhat. With the motor shut off and with increase in elongation, the stress on the rubber and dynamometer decreased steadily and prevented the determination of the exact laws concerned. Accordingly in some cases the motor and dynamometer were replaced by a simple cord on a pulley with a weight, which had the advantage of making possible the application of a steady invariable stress and, hence, reliable determinations of the laws.

The flow phenomena were particularly evident at low temperatures, so it seemed advisable to carry out extensive measurements at these temperatures. At these low temperatures, alcohol containing solid carbon dioxide was used as the medium. The tensile apparatus was surrounded to as great an extent as possible on all sides by this alcohol bath, with particular care not to allow the rubber test-specimen to come in contact with the alcohol. By using a metal container with thick walls (see Figure 1c), a uniform temperature was assured throughout the interior of the apparatus. The apparatus shown open in Figure 1c was covered over during a test with a metal trough, which likewise contained cold alcohol. The whole assembly was then packed in layers of Iporka to insulate it thermally. The tension rod was thus the only connection

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to the motor and dynamometer. It was found, however, that the experimental measurements deviated considerably from their normal dependence on the temperature because of the thermodynamic warming of the rubber when stretched[4], due to the Gough-Joule effect. It was necessary, therefore, to immerse the test-specimen itself in the cold alcohol bath with which the middle container (that heavily outlined in Figure 1c) also was filled. This made it certain that the rubber test-specimen was brought immediately to the required temperature, and that it would remain at that temperature. The test-specimen itself was in the alcohol bath only a quarter of an hour during the actual

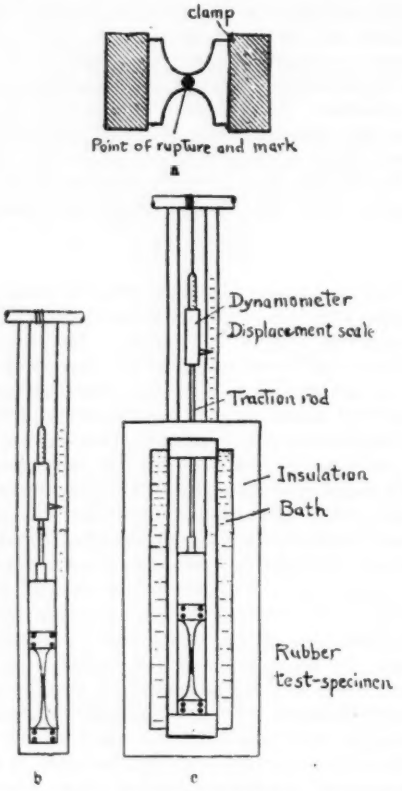

FIG. 1.—Test of tensile properties. a.—Died-out test-specimen (1 : 2.5 natural size). b.—Apparatus. c.—Apparatus for low temperatures[5].

measurement. It was found in preliminary tests that twelve hours' immersion in the alcohol bath at room temperature did not alter the stress-strain curve nor the tensile strength.

METHOD OF EVALUATION

The elongation E is determined very simply by the drawn out printed mark on the test-specimen, *i.e.*, by the ratio of the new dimension at any reading to

its original diameter. When defined in this way, the elongation has the advantage of being easily calculated, *i.e.*, if the original value is 1 and the change in length is Δl in the theory of elasticity, then the following relation holds:

$$E = \frac{l}{l_0} = \frac{l_0 + \Delta l}{l_0} = 1 + \frac{\Delta l}{l_0} \tag{1}$$

The increase in length, expressed in percentage, as is usually done technically, is $(E - 1) \times 100$. In this case, elongation always means linear elongation, whereas surface extension equally in all directions would be represented by E^2.

To determine the stress $\bar{S}_0$, the applied force F is divided by the original cross-section of the test-specimen:

$$\bar{S}_0 = \frac{F}{t_0 w_0} \tag{2}$$

where t_0 is the thickness and w_0 the width of the test-specimen. This stress $\bar{S}_0$ is frequently used in technical measurements but, as pointed out in detail in earlier work[6], this stress has no physical significance independent of the method of measurement, and can be used only as a basis of comparison. On the other hand, the force F refers to the cross-section at the particular moment, and therefore by definition gives the true stress S.

In the earlier work mentioned[7], it was shown that the following relation holds true:

$$S = \bar{S}_0 \cdot E \tag{3}$$

Since the change in shape of the imprinted mark and, consequently, the elongation at low temperatures could not be observed directly, it was necessary under these conditions, in determining the tensile properties, to measure the displacement of the rigid tension rod outside of the apparatus, and then, from the curves obtained at normal temperature relating elongation to the displacement of the rod, to estimate the elongations at low temperatures. In such an interpolation, it was, of course, assumed that, even at low temperatures, the shape of the deformed rubber test-specimens was always similar to that of those tested at normal temperature.

RESULTS

Following the procedure described, a series of rubber samples was tested, and it was found that all behaved in the same way. It was necessary, therefore, in studying such a series, to study only one member in detail. To this end Igetex-S, a product manufactured from a Buna-S latex by the Pongs Company of Aachen, was chosen.

Figure 2 shows the stress $\bar{S}_0$ as a function of the elongation E at various temperatures. The linear relationship between $\bar{S}_0$ and E which was to be expected on the basis of Hooke's law was found to hold true only within a limited range. It will be seen that the curves for higher elongations and, in turn, for low temperatures, are steeper and reach higher $\bar{S}_0$ values. During an experiment the apparatus was stopped for making measurements at the desired points. It was found in this way that, at certain temperatures, there was a surprising flow of the rubber. As is characteristic of all amorphous materials, slow flow occurred at room temperature, but at low temperatures this flow was much more rapid. Because of the change in length resulting

from this flow, there was a relaxation of the stress when the motor was stopped. The elongation and stress were recorded after about one minute, and the measurements were continued after increasing the stress. In this way, the zig-zag curves in Figure 2 were obtained, the sloping broken lines of which represent in their inclination the characteristic line of the tensile apparatus[9].

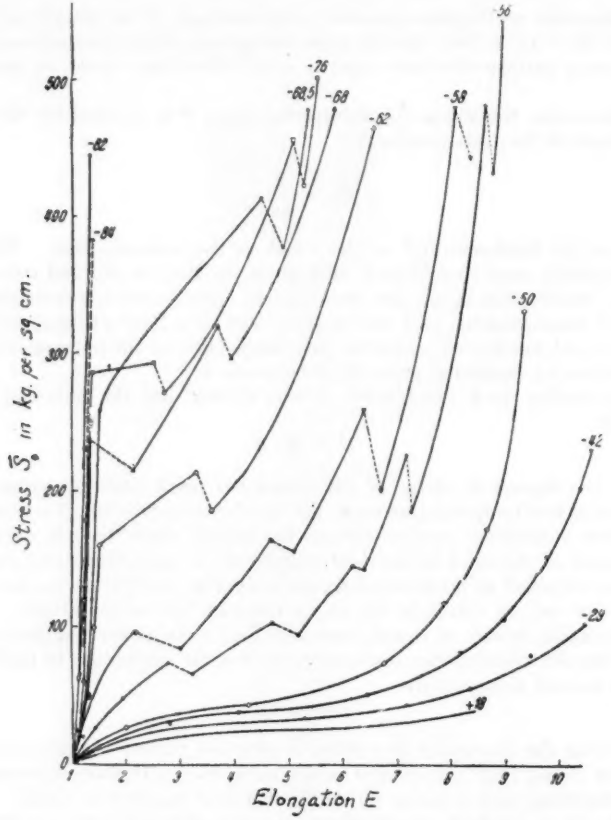

FIG. 2.—Stress-strain diagram of Igetex-S at low temperatures. The stresses are based on the original cross-section. The temperatures are in degrees Centigrade. The points of measurement shown on the diagram represent in all cases breaks in the curves. The broken lines represent flow at the particular temperatures[8].

In comparison with the total elongation, this flow phenomenon was slight. However, the tensile measurements lasted only a few minutes, and therefore in a further evaluation the curves were constructed smooth without the steps shown in Figure 2. By multiplying the individual stress $\bar{S}_0$ measurements by E, in accordance with Equation (3), the changing thickness of the test-specimen was taken into account, and the S stress curves shown in Figure 3 were obtained.

Considering now the behavior at the moment of rupture, the curves shown in Figure 4 for the ultimate elongation and those shown in Figure 5 for the tensile strength were obtained. In addition to Igetex-S, natural rubber and Perbunan, further data on which will appear later, are included. The behavior of all three types of rubber at low temperatures can be characterized schematically in the same way. The elongation at rupture is, within a certain low temperature range, relatively low, while in another range of much lower temperatures it is very low and practically independent of the temperature.

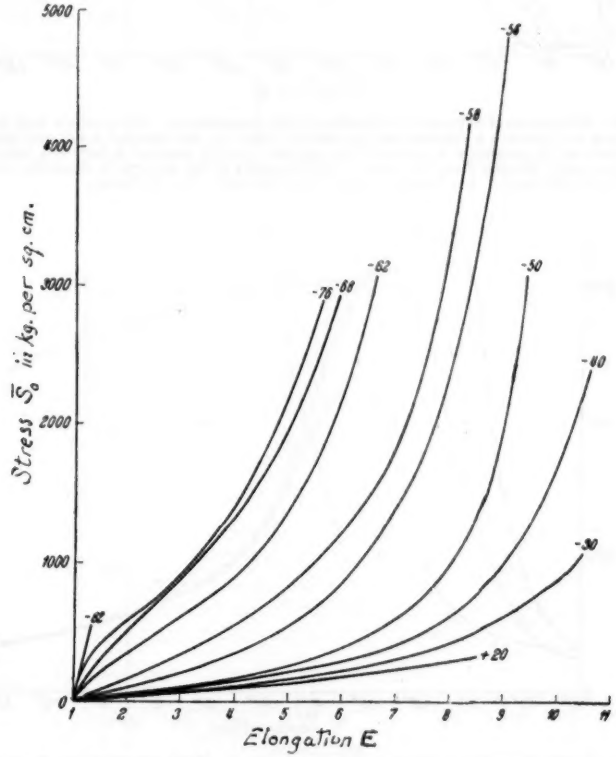

FIG. 3.—Stress-strain diagram of Igetex-S at low temperatures. In distinction to the data in Figure 2 the stresses are based on the cross-section at the particular elongations. The temperatures are in degrees Centigrade. The insignificant flow which took place in the brief time intervals was disregarded, and the curves represent mean values.

Between these two ranges the elongation decreases rapidly with lowering of temperature, *e.g.*, natural rubber changes from a soft elastic material to a hard inelastic material. On comparing all the experimental results, and, in particular, on comparing the temperature range where the elongation decreases so rapidly with other properties of these elastomers, it will be found that, for all three elastomers, this temperature range represents the range in which cold flow and, at the same time, stiffening take place. At the limits of this range

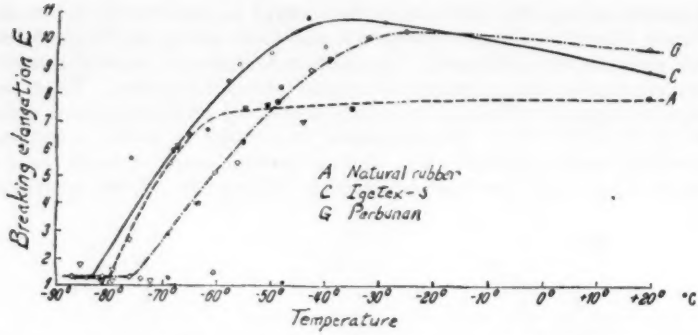

FIG. 4.—Elongation at rupture as a function of the temperature. At relatively high temperatures the elongation at rupture is a constant and is relatively high, i.e., the material is soft and elastic; at very low temperatures the elongation is constant but very low, i.e., the material is hard and inelastic. There is a transition range between these two states. The beginning of this decrease in elongation represents the temperature of stiffening[10]. A.—Natural rubber. C.—Igetex-S. G.—Perbunan.

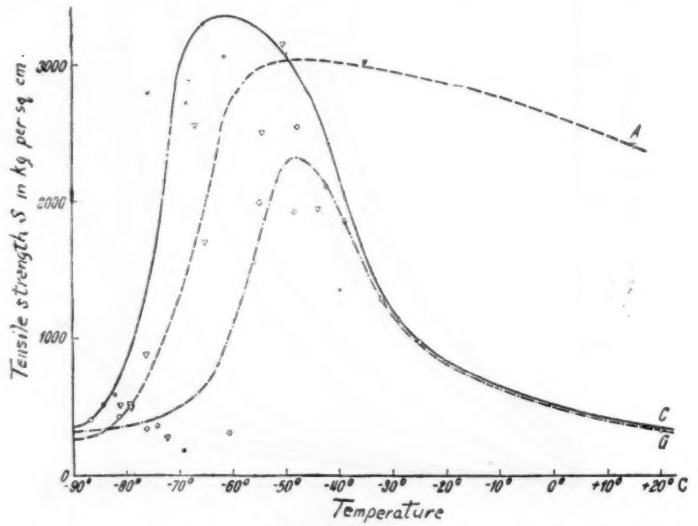

FIG. 5.—Tensile strength as a function of the temperature. When calculated on a basis of the cross-section at the particular elongations, the tensile strength as a function of the temperature shows a maximum value at some particular temperature[11]. A.—Natural rubber. C.—Igetex-S. G.—Perbunan.

flow is slight and therefore more difficult to observe. In any case, the point where the elongation at rupture shows the first evidence of decreasing is of fundamental importance in characterizing a rubberlike material. This particular temperature may be designated as the stiffening temperature.

THE FLOW PHENOMENON

After this initial attempt at orienting the phenomena of cold flow, the laws of flow of Igetex-S were studied systematically. Because of the fact that one

definite load was used, the apparatus was equipped with a weight. When the test-specimen was loaded with this weight, an initial elongation took place in every case, but this soon came to a stop. On the other hand, appreciable cold flow took place above a certain loading, and the extent of this flow depended greatly on the temperature. In Figure 6 this yield point is shown as a function of the temperature. The minimum value of the yield point is at $-53°$ C.

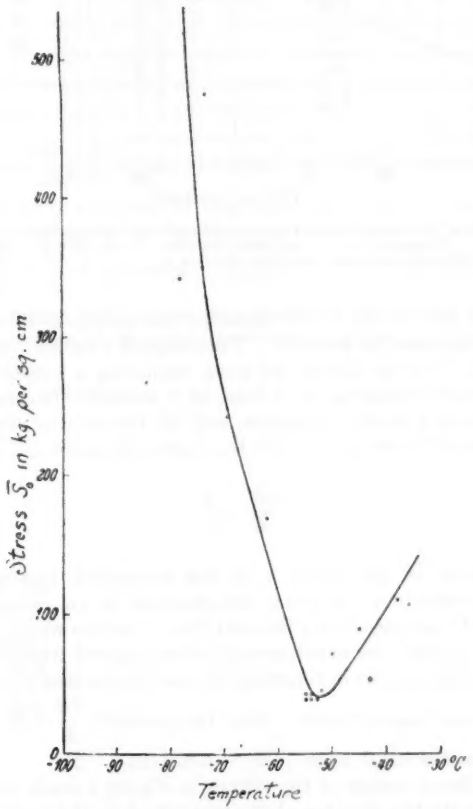

FIG. 6.—Yield point of Igetex-S is a function of temperature in experiments where the stress was applied as a weight. The stress (based on the original cross-section) at which flow begins as a function of the temperature.

The course of the right branch of the curve is somewhat uncertain, because within this range of temperature there is considerable elongation superposed on the flow phenomenon.

When the load is greater than that corresponding to the yield point, continuing flow sets in. Figure 7 shows this phenomenon as a function of time. Representation on a logarithmic scale gives fairly accurately a straight line, so that the following law applies:

$$E = a \cdot \ln t + E_0 (1 \leqq t \leqq \infty) \tag{4}$$

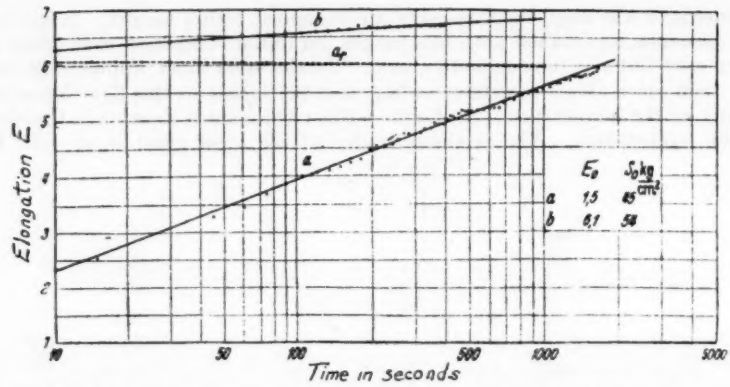

FIG. 7.—Elongation by flow of Igetex-S as a function of time in experiments where the stress was applied as a weight. Elongation as a logarithmic function of the time at −52° C. a.—$E_0 = 1.5$. b.—$E_0 = 6.1$. a_r = relaxation on release of stress after flow a.

Although the time factor in this equation has no significance, it should as a general rule be expressed in seconds. The range of t values must obviously be restricted to $t \geqq 1$ to the factor $\ln t$ from becoming a constant value[12]. E_0 and a refer, strictly speaking, to a time of 1 second. Because of the small change in E during 1 second, however, and for the sake of clarity, the initial value of zero should be retained. On this basis, Equation (5) is equivalent to Equation (4):

$$\frac{dE}{dt} = \frac{a}{t} \tag{5}$$

The dependence of the factor a on the elongation was studied by first stretching a test-specimen at room temperature to an elongation E_0, then cooling to −52° C and measuring the cold flow. In this way a yield point was obtained which, within the experimental errors, agreed with the other value. On the contrary, the a value in Equation (5) was in this case very different from that of the previous measurement. Only the product: $\frac{dE}{dt} \cdot t \cdot E_0 = a \cdot E_0$ had in both cases almost the same value ($aE_0 \sim$ constant).

The strictly linear course of the curves in Figure 7 leads inevitably to the conclusion that only the E value at the instant when the load is first applied, *i.e.*, the E_0 value, plays any part in the phenomenon.

In addition, it would be expected that there would be a dependence on the applied stress $\bar{S}_0$, and, above all, a proportionality with $\bar{S}_0$ might be assumed.

TABLE 1

INFLUENCE OF ELONGATION

ϑ (° C)	E_0	$\bar{S}_0$ (kg. per sq. cm.)	a	aE_0
−52	1.1	40	0.35	0.39
−52	7.4	44	0.03	0.22

TABLE 2

INFLUENCE OF LOAD

ϑ (°C)	E_0	$\bar{S}_0$ (kg. per sq. cm.)	$\frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0}$
−52	1.1	40	0.0096
−52	2.4	178	0.0081
−52	8.0	178	0.0090
−52	8.2	178	0.0092
−53	1.5	46	0.023
−53	6.1	54	0.014
−53	6.7	77	0.017
−53	7.4	132	0.014

The expression: $\frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0}$ must, therefore, be constant, and this was verified experimentally, as can be seen by examining the data[13] in Table 2.

Finally the influence of the temperature remained to be investigated. If the factor $\frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0}$ is plotted as a function of the temperature, as in Figure 8, it is seen to increase with rise in temperature. In view of the closely corresponding trend of the yield point in reverse, as shown in Figure 6, multiplica-

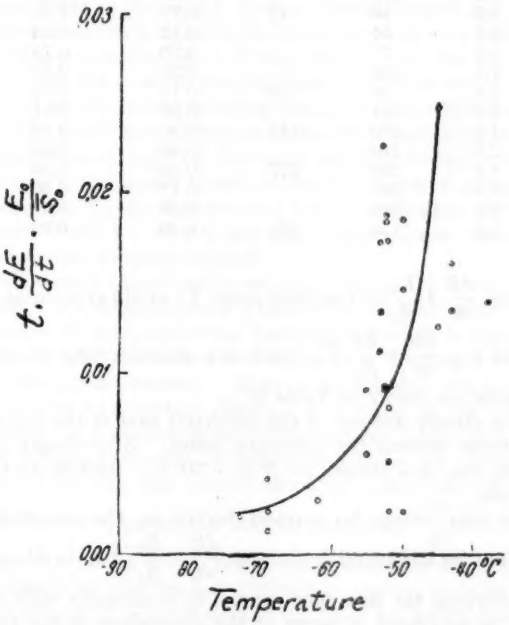

FIG. 8.—Flow properties of Igetex-S as a function of the temperature in experiments where the stress was applied as a weight. The factor $\left(t \cdot \frac{dE}{dt} \cdot \frac{E_0}{\bar{S}_0} \right)$ (elimination of time t, initial elongation E_0, and stress S_0) as a function of the temperature.

TABLE 3

INFLUENCE OF THE TEMPERATURE

Temperature (° C)	E_0	$\bar{S}_0$	$\bar{Y}_0$	$\frac{dE}{dt} \cdot t$	c	c_{mean}
15	7	30	40	0.015	0.14	0.14
	2.5	30		0.0048	0.016	0.12
				0.070	0.23	
				0.034	0.30	0.30
				0.040	0.35	0.35
				0.014	0.068	
				0.15	0.73	0.40
					Mean	0.26
					Deviation	0.13
−38	9.2	111	40	0.17	0.56	
−43	1.1	64	40	0.25	0.18	
	7.5	110		0.20	0.55	
	8.5	156		0.30	0.64	
−45	7.5	90	40	0.30	1.00	
	8.1	160		0.25	0.50	
−50	6.8	73	48	0.20	0.89	
	8.6	155		0.30	0.71	
−52	1.1	40	42	0.35	0.39	
	2.4	178		0.62	0.35	
	8.0	178		0.20	0.38	
	8.2	178		0.20	0.39	
−53	1.5	46	42	0.77	1.05	
	6.1	54		0.12	0.56	
	6.7	77		0.20	0.78	
	7.4	132		0.25	0.59	
−55	1.1	40	56	0.14	0.22	
	2.3	151		0.60	0.51	
−62	1.0	170	145	0.50	0.43	
	2.9	270		0.40	0.62	
−69	1.4	243	227	0.43	0.56	
	2.5	243		0.12	0.30	
	3.1	300		0.40	0.94	
−73	2.5	476	325	0.40	0.69	

tion of the factor, $\frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0}$ by the yield point $\bar{Y}_0$ would give, in an approximate way, a constant $c = \frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0} \cdot \bar{Y}_0$ which is a characteristic of every material. These calculations are shown in Table 3.

Of course the steady descent of the left-hand part of the curve in Figure 6 must then continue beyond the minimum point. Accordingly a value of $\bar{Y}_0$ of 40 kg. per sq. cm. was chosen for $\vartheta \leqq -50°$ C. Justification for this will be discussed later.

It is evident that, except for marked deviations, the expected results were obtained. Except for incidental deviations, $\frac{dE}{dt} \cdot t \cdot \frac{E_0}{\bar{S}_0} \cdot \bar{Y}_0$ is in all cases equal to c.

The law governing the flow phenomena, in conformity with requirements, can, therefore, be expressed in terms of the dimensions in the following way:

$$\frac{dE}{dt} = c \cdot \frac{\bar{S}_0}{E_0 \cdot t \cdot \bar{Y}_0} \tag{6}$$

The function a introduced in Equation (5) is, consequently, not a constant, but is a function of E_0, $\bar{S}_0$, and $\bar{Y}_0$, thus: $a = c \cdot \frac{\bar{S}_0}{E_0 \cdot \bar{Y}_0}$. With time, and also on repeated stressing to higher elongations, therefore, the rate of flow becomes progressively smaller. In contrast to the earlier work[1], the factors involved in the initial state are of real significance, since they have an influence on the integral flow phenomena (see the comment following Table 1). Any further calculations were, therefore, given up. Since $\bar{S}_0$ and $\bar{Y}_0$ are related to each other only as a ratio, it was possible to use the expression: $\bar{S}/\bar{Y}$, as well.

With respect to the validity of the equation above, it should be remarked that $\bar{S}_0$, E_0, and $\bar{Y}_0$ are in many cases related only in a qualitative sense, and since flow phenomena frequently depend on chance structural features of a material, no such exact law as applied to other more sharply defined natural phenomena should be expected of such flow phenomena.

Of special importance are the measurements at room temperature. In this case the flow phenomena were followed for a particularly long time, viz., up to 7000 seconds, and the measurements were evaluated as before. As can be easily understood, because of the small $\bar{S}_0$ values, the friction of the slide in the apparatus plays a significant part in the measurements and makes the c values inaccurate. This is true also of yield point, $\bar{Y}_0$, which, as already mentioned, was only extrapolated roughly. For these reasons, the mean value of these c values was used.

In many cases c was at first small, then suddenly jumped (as shown by the break in the curve showing a logarithmic time function) to a value such that the mean fell within the normal order of magnitude. It is worthy of note that, at room temperature, the c values are the same within the range of deviations as the values at low temperatures, showing that the same underlying phenomena in both cases. The small and, therefore, difficultly observable rate of flow at room temperature depends only on the much smaller stresses, which must, of course, remain below the small tensile strengths at room temperature. At room temperature, $\bar{S}_0/\bar{Y}_0$ lies between 0.4 and 0.7; whereas at low temperatures it is between 1 and 4. At low and high temperatures, therefore, a test-specimen may show far different stresses.

A thermodynamically important question is that of the reversibility of this flow phenomenon. If a test-specimen is allowed to flow for some time and the load is then reduced to zero, retraction takes place, which is rapid during the first few seconds and then becomes slow. In general the longer the flow under stress, the less is the initial recovery. After prolonged flow, the elongated state is obviously stabilized to a certain degree. According to the schematic diagram of Houwink[14], the initial retraction phenomenon would be a spontaneous plastic recovery; the subsequent retraction would be an elastic secondary effect. The law governing this elastic effect as a function of time would, therefore, be that of flow, except for smaller constants: $\frac{dE}{dt} \cdot t \sim 0.01$–$0.2$ (see curve a_r in Figure 7). A law which takes into account the other factors in this recovery phenomenon is possible but difficult to derive, because in this case many incidental effects, of greater magnitude than are encountered in extension, in the structure of the material, play a part in the recovery.

As soon as a new load is applied to a test-specimen after it has relaxed, as described above, the E_0 value at the beginning of this new measurement

must be used. The different E_0 values shown in Tables 2 and 3 and curve b in Figure 7 were obtained in this way.

In a special experiment with a view to determining whether the laws were still valid, and also to verify whether the same phenomena take place during ascent of balloons, a very small initial load was applied every minute by the same constant additional load g. Accordingly in Equation (6) $\bar{S}_0(1 + \kappa t)$ must be substituted for $\bar{S}_0$ if $g/60 = \kappa \cdot S_0$. Then:

$$\frac{dE}{dt} = \frac{d \cdot \bar{S}_0}{E_0 \cdot \bar{Y}_0}\left(\frac{1}{t} + \kappa\right)$$

Integration to avoid a single value of ln at the lower limit 1, gives:

$$E - E_1 = \frac{c \cdot \bar{S}_0}{E_0 \cdot \bar{Y}_0} \cdot [\ln t + \kappa(t - 1)]$$

In an approximate calculation, a time as short as 1 second can, as before, be disregarded. Hence:

$$\left.\begin{aligned} E - E_0 &= \frac{c \cdot \bar{S}}{E_0 \cdot \bar{Y}_0}[\ln t + \kappa \cdot t] \\ &= a[\ln t + \kappa \cdot t] \end{aligned}\right\} \qquad (7)$$

Therefore the elongation, in accordance with Equation (4) and Figure 7, increases linearly with time.

In one experiment, carried out at $-53°$ C, this difference for

$$E - [E_0 + a \cdot \ln t] = E - E^* = a \cdot \kappa \cdot t$$

in the first seven minutes showed a linear increase with time, with the factor $a \cdot \kappa_1$, which subsequently flattened and became $a \cdot \kappa_2$ (see Figure 9). From the increase during the first minute, a was calculated to be 0.22, and hence $\kappa_1 = 0.045$, and $\kappa_2 = 0.005$. On the contrary, for the applied load $g = 0.1$ kg., and $\bar{S}_0 = 0.58$ kg. per sq. cm., according to Equation (7), $\kappa = 0.0029$, which is one-twentieth and one-half, respectively, that calculated by measuring the elongation.

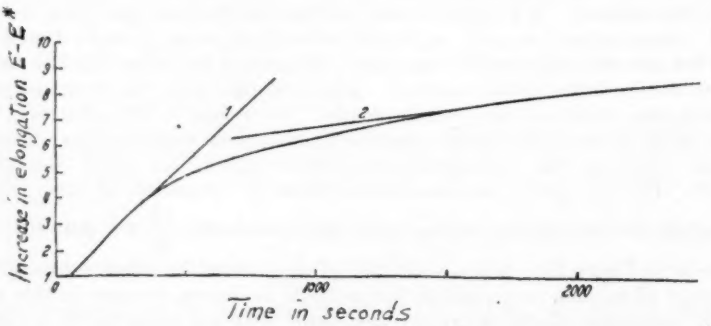

FIG. 9.—Additional elongation of Igetex-S at $-53°$ C with a steadily increasing load. The initial elongation and the flow resulting from the initial load are expressed by E^* in the deduction. E–E^* is shown as a function of time. The required linear increase in elongation is fulfilled only at the beginning and at the end of the process, and the increase does not conform to the additional weight.

$\bar{S}_0 = 0.50$ kg. per sq. cm. $\qquad g = 0.1$ kg.

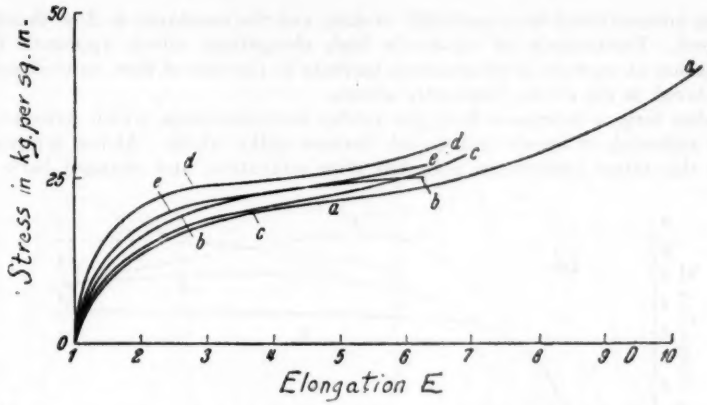

FIG. 10.—Stress-strain diagram of test-specimens of Igetex-S allowed to flow at room temperature (18° C). The stresses are based on the initial cross-section. The pretreatment differed (comparison of flow with preliminarily stressed and not stressed test-specimens).

No.	Preliminary treatment	E	Temperature
a	none	—	18° C
b	prestressed	7	18° C
c	flow	9.8	−51° C
d	flow	11	−43° C
e	flow	4.3	−68° C

This behavior is in agreement with the generally observed and already mentioned fact that the dependence of the flow phenomenon on the stress is in general proportional only to S_0, but that, in individual experiments, deviations from this rule are often encountered. This also explains the marked deviation in Table 3. A break in the curve can occur quite suddenly, and the flow continue with much greater rapidity. It would appear, therefore, as if a

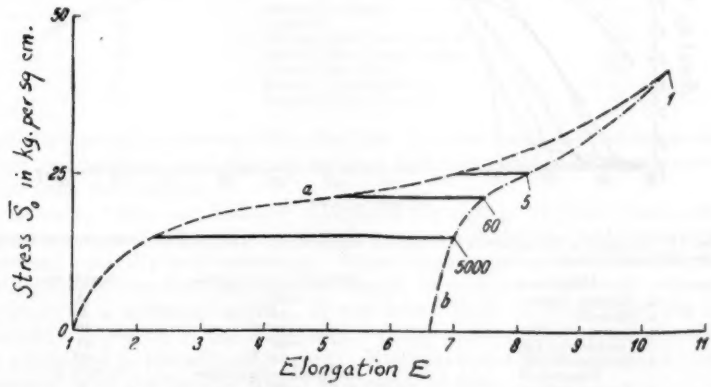

FIG. 11.—Stress-strain diagram of tensile strength and flow of Igetex-S, with and without deadweight loading, at room temperature (18° C). The stresses are based on the original cross-section. a.—Curve for short time. Reduction in breaking elongation as a result of flow (curve b). Duration in minutes of experiments to the points of rupture are indicated on curve b (1, 5, 60, and 5000).

– – – Stressing with motor
—— Stressing by dead-weight load
— · — Breaking elongation by flow

strong internal bond were suddenly broken, and the resistance to flow thereby lessened. Particularly at relatively high elongations which approach the elongation at rupture, a spontaneous increase in the rate of flow, as evidenced by a break in the curve, frequently occurs.

After long or extensive flow, the rubber test-specimens, which were originally yellowish or brown and turbid, became milky white. At low temperatures this latter appearance persisted after relaxation, and changed back to

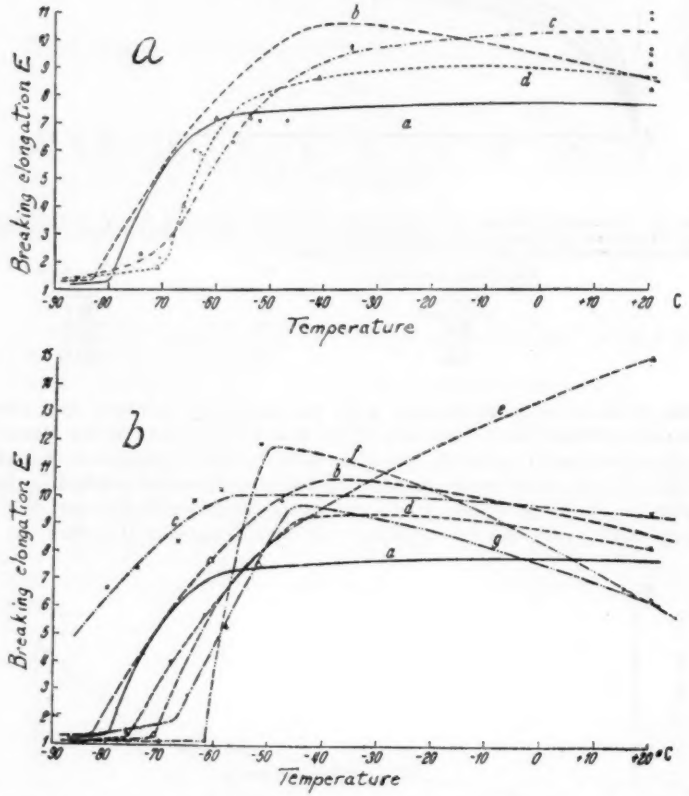

FIG. 12.—Elongation at rupture as a function of temperature. This diagram corresponds to Figure 4, but is for different materials.

Diagram A	Stiffening temperature	Sample no.
a. Natural rubber	−59° C	A
b. Igetex-S	−43° C	C
c. Oppanol-G (x)	−48° C	40
Oppanol-IG (o)	−48° C	41
d. Oppanol-W (Δ)	−54° C	42
Diagram B	**Stiffening temperature**	**Sample no.**
a. Natural rubber	−59° C	A
b. Igetex-S	−43° C	C
c. Natural latex (unvulcanized)	−60° C	43
d. Natural latex compounded	−45° C	44
e. Buna-S (raw film)	—	45
f. Buna-S (vulcanizate B)	−51° C	47
g. Buna-S (vulcanizate A)	−48° C	48

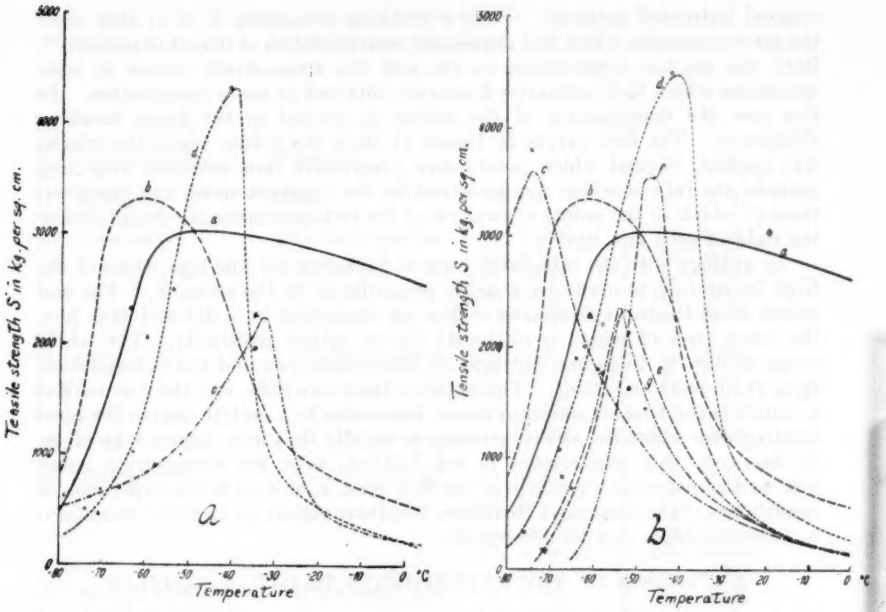

FIG. 13.—Tensile strength as a function of temperature. These diagrams correspond to Figure 5, but are for different materials.

Diagram A	Material	Sample no.
a.	Natural rubber	A
b.	Igetex-S	C
c.	Oppanol-G (x)	40
d.	Oppanol-IG (o)	41
d.	Oppanol-D (Δ)	42

Diagram B	Material	Sample no.
a.	Natural rubber	A
b.	Igetex-S	C
c.	Natural latex (unvulcanized)	43
d.	Natural latex (compounded)	44
e.	Buna-S (raw film)	45
f.	Buna-S (Vulcanizate B)	47
g.	Buna-S (Vulcanizate A)	46

turbid yellowish or brown only after the test-specimens had been warmed to room temperature, and thereby became indistinguishable in appearance and color from the original.

Scheele, Alfeis and Lahaye[15] compared the change in color when softening agents were removed from one of their synthetic materials, which was thereby rendered optically heterogeneous. Accordingly experiments were carried out with Buna-S, raw-film, and natural latex[16], in each case with and without the addition of a softening agent. It was found that, in every case, the milky turbidity appeared in the same way. Consequently the turbidity could not be attributed to the softening agent. Even several different types of Oppanol changed color and became turbid as a result of flow.

Accompanying the flow phenomenon is a deterioration of the mechanical properties of the rubber. Test-specimens which had undergone flow at low temperatures were, after relaxation and warming, considerably less extensible than originally, and only in this way could they be distinguished from the

original untreated material. With a breaking elongation E of 7, they were the same as samples which had previously been stretched at room temperature[17]. Both the normal stress-strain curves and the stress-strain curves of test-specimens which had undergone flow were obtained at room temperature. In this case the deterioration of the rubber is evident in the lower breaking elongation. The flow curves in Figure 11 show the points where the weight was applied, beyond which points slow progressive flow occurred over long periods, the rate of which was governed by the constant stress and the durations of which to the points of rupture of the test-specimens are designated at the right of each flow line.

In analogy with the integrated form of Equation (6), the logarithms of the time for rupture to occur are roughly proportional to the stress $\bar{S}_0$. The end points of all the individual lines of flow are connected by a dot-and-dash line, the lower part of which is obviously drawn rather arbitrarily. The whole range of flow is, therefore, outlined by the broken line and the dot-and-dash line, which meet at a point. The upper of these two lines, *i.e.*, the one marked *a*, which is the true stress-strain curve, represents to a certain degree the ideal limiting case where the stress increases so rapidly that flow cannot take place. If, however, this requirement is not fulfilled, then the stress-strain curve follows a course somewhere within the flow area, according to the experimental conditions. It is necessary, therefore, to adhere rigidly to specified conditions in order to obtain comparable results.

EXTENSION OF THE EXPERIMENTS TO OTHER SAMPLES

A more thorough study of other types of rubber by the dead-weight method of flow could not be undertaken for reasons not related directly to the work. However, some samples were tested according to the methods shown in Figures 2, 4, and 5, and the results of the elongation and tensile strength measurements are shown in Figures 12 and 13. The materials tested included various types of Buna, with and without softening agent, and vulcanized and unvulcanized, and also several types of Oppanol, which were particularly plastic at room temperature (see Table 4). Only a few points were measured, so the course of the curves is not so well defined as in Figures 4 and 5. Sample no. 43, which was unvulcanized natural-rubber latex with no addition, showed particularly great deviations compared to the other samples. The corresponding measurements shown in Figure 2 were made at the end of exactly one minute by means of a stopwatch, and therefore they make it possible to compare, at least in an approximate way, the various types of material on a quantitative basis.

By integration of Equation (6) between the time limits of 1 and 60 seconds, the change in elongation in this time interval is:

$$\Delta E = E_{60} - E_1 = c \cdot \frac{\bar{S}_0}{E_0 \cdot \bar{Y}_0} \cdot \ln 60$$

For the reasons already explained:

$$\Delta E = E_{60} - E_1 \sim E_{60} - E_0$$

From the experimental data, the factor $\frac{\Delta E \cdot E_0}{\bar{S}^0} = C$ can be determined in some cases; it is related to the desired c value as follows:

$$c = \frac{C \cdot \bar{Y}_0}{\ln 60} = \frac{\Delta E_0 \cdot E \cdot \bar{Y}_0}{\bar{S}_0 \cdot \ln 60} \qquad (8)$$

TABLE 4

FLOW CONSTANTS

No.	Material	Source	Temperature (° C)	C	No. of measurements	$\bar{P}_0$	c	c_{mean}
A	Natural rubber	Delacoste	—	—	—	—	—	—
C	Igetex-S	Pongs	−57	0.0111	10	80	0.21	0.21
40	Oppanol-G	I.-G. Ludwigshafen	−35	0.0089	4	32	0.07	
			−52	0.032	3	45	0.35	
			−63	0.017	3	84	0.34	0.17
			−70	0.00091	3	175	0.039	
			−79	0.00047	1	320	0.037	
41	Oppanol-GI	I.-G. Ludwigshafen	−35	0.0047	4	32	0.037	
			−47	0.043	3	40	0.42	
			−58	0.023	3	45	0.31	0.23
			−64	0.0077	4	95	0.18	
			−74	0.0031	3	245	0.18	
42	Oppanol-W	I.-G. Ludwigshafen	−41	0.023	5	21	0.12	
			−54	0.012	4	35	0.10	
			−60	0.013	6	58	0.18	0.14
			−66	0.0058	3	115	0.16	
			−71	0.00041	2	185	(0.019)	
43	Natural latex with no addition and unvulcanized	I.-G. Ludwigshafen	−59	0.027	5	13	0.086	
			−64	0.027	5	22	0.14	
			−67	0.043	3	29	0.30	0.18
			−75	0.00083	5	61	0.12	
			−80	0.010	5	103	0.24	
44	Natural latex loaded and vulcanized	I.-G. Ludwigshafen	−42	0.011	5	25	0.066	
			−58	0.019	6	46	0.21	
			−62	0.0058	4	72	0.10	0.12
			−68	0.0046	2	140	0.16	
			−76	0.00070	1	290	0.049	
45	Buna-S (raw film)	I.-G. Ludwigshafen	−30	0.061	2	16	0.24	
			−52	0.012	4	38	0.11	0.18
			−61	0.012	3	65	0.19	
			−71	0.0011	1	155	(0.041)	
46	Buna-S (vulcanized)	I.-G. Ludwigshafen	−48	0.012	3	62	0.19	
			−58	0.0073	2	145	0.26	0.23
			−65	0.0043	1	238	0.25	
47	Buna-S (vulcanized)	I.-G. Ludwigshafen	−49	0.015	3	68	0.25	0.32
			−52	0.018	3	89	0.38	

A mean value for the stress was used for $\bar{S}_0$. The necessary yield points were derived from the $\bar{S}_0$ values representing the points where flow began, and they are shown in Figure 14. Obviously they give only a rough idea of the facts. Table 4 summarizes all the results obtained with the various samples. The c and C values are the mean values of various measurements. As a test of the method, additional measurements of Igetex-S were made, following the method shown in Figure 2, at one temperature, and at the end of exactly one minute. A comparison of the two c values for Igetex-S in Tables 3 and 4 shows that the two methods give results which are in agreement within the

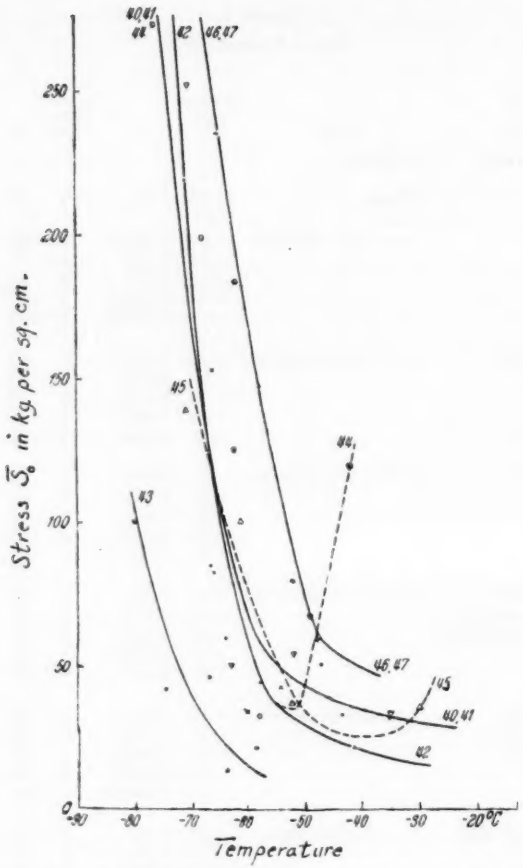

FIG. 14.—Yield point as a function of temperature in experiments with dead-weight loading. Stresses at the beginning of flow as a function of the temperature for various materials. The stresses are based on the original cross-section.

Sample no.

▽ 40	x 42	□ 44	+ 46
● 41	o 43	△ 45	◇ 47

limits of deviation and, therefore, that calculations by means of Equation (8) are justified. The c values of all the materials are of the same order of magnitude, whether the materials were vulcanized or unvulcanized.

INTERPRETATION OF THE PHENOMENA BY MEANS OF A MODEL

In the testing of rubber at low temperatures, the stiffening which takes place on short exposure (see Figure 5) and the accompanying flow brought about by the application of prolonged stressing seems at first to be a rather surprising combination of properties; in fact, the two phenomena seem to contradict the usual concepts of substances which have been designated as being in a microliquid state. According to Müller[18] this state is characterized

by the fact that the material behaves like a liquid if it is subjected to a mechanical stress within very small dimensions, whereas it behaves like a solid if the mechanical stress is applied to the material as a whole. Therefore it is necessary to picture the intermolecular forces as predominating over the intramolecular forces[19].

In the case of rubber this predominance depends on the chain form of its molecules. The free diffusion and resultant migration of the molecules are hindered in comparison to the behavior of an ideal liquid; in contrast to the latter, the external form of the molecules is retained. This hindering effect is further increased by polymerization or by vulcanization as a result of the chains forming a network structure. On the other hand, the great degree to which rubber is deformed by relatively small stresses is explained by the ease of mutual displacement, as in a liquid, of the chain members lengthwise. As a result of their thermal movements, vibration, and rotation, the chains collide with one another. With such unilateral motion, the strain becomes unilateral, and forces are set up which, on release of the stress, tend to cause retraction of the deformation.

In this way the high elastic behavior of rubber can be explained[20]. According to what has been said, high elasticity is obviously possible only if the molecular chains vibrate in contact with one another and there is intramolecular micromovement. On the other hand, it is necessary that there be a certain degree of stability of the whole structure and, consequently, a hindrance of intermolecular macromovement. In the language of Kuhn, the time of relaxation of the micromovements must be small and that of the macromovements must be relatively great. Both these conditions can be fulfilled simultaneously, if at all, only within a certain range of temperature. In addition to the already frozen macromovements involved in the present work, too low temperatures allow the freezing of the micromovements in proportion to their energy requirements.

The liquid state reverts to the solid state in rubber, until the latter finally becomes an ordinary solid material in the amorphous state. On the other hand, too high temperatures increase the macromovements so greatly that they endanger the cohesion of the network (the case of softening between 100° and 200° C is not considered here). Accordingly rubber passes through three states from high to low temperatures, *viz.*, viscous liquid, highly elastic microliquid, and amorphous solid.

Since in rubber the distribution of forces which control the migration do not, as in an ideal crystal, show a periodic course in potential, but, on account of the amorphous state, an irregular change from high to low points of different heights and depths, it is understandable why the transformation from the microliquid state (the upper horizontal parts of the curves in Figure 4) to the amorphous solid state (lower horizontal parts in Figure 4) takes place, not suddenly at a definite temperature as in the case of crystals, but through a whole range of temperatures. Likewise it is understandable why forces which are too small to bring about rupture of the material are, nevertheless, sufficient to cause flow by overcoming flatter potential waves. In this process of flow, certain conditions are so altered that an irreversible deterioration, as manifest in loss of breaking elongation, takes place, as shown in Figures 10 and 11.

When a stress is applied at room temperature, an almost steady progressive deformation and accompanying stiffening of the material take place. These phenomena must be related to the formation of a partially crystalline structure during elongation[21]. As the chains straighten out, the course of the potential

becomes more regular and the tension is compensated by the elongation, so no stress is any longer available for flow. Only in the region of the breaking elongation, *i.e.*, at high elongations and loads, when the structure has been loosened, can any notable flow occur, as in every crystal. Such a condition is, however, to be distinguished from the flow in the present work. These considerations apply to the microliquid state, where a deformation soon follows a stress. On the other hand they do not apply to the transformation interval. In this case, the elongation does not immediately reach its final value, and a residual stress remains, and therefore the flow becomes more pronounced. The longer it continues, however, the more is the applied force compensated, and the smaller is the recovery after release of the stress (see curve a_r in Figure 7).

Every stress which is applied supposedly causes flow. Because of the very high viscosity, however, flow of any practical significance takes place only above a definite stress, which is the yield point. For the amorphous solid state, this yield point is naturally particularly high. The greater the thermal micromovement of the chains, the lower is the yield point. Therefore the yield point would be expected to depend on the temperature in accordance with the Boltzmann law:

$$\frac{1}{\bar{Y}_0} = A \cdot e^{-E/k \cdot T} \tag{9}$$

An evaluation of the left-hand part of the curve in Figure 6 gives the relatively high and naturally very uncertain energy value of E = 0.3–0.4 V. In this part of the curve of the transformation, the elongations lie in the range of 1 to 2. On the contrary, in the right-hand part of the curve, which has so different a course, the elongations range from 7 upward. This is the case shown above, which is no longer concerned with the transformation period, but with the microliquid range[22]. Rubber yields under stretching and consequently with rising temperature and resulting softening, the yield point approaches the breaking elongation. An entirely different phenomenon is therefore involved; hence the decision not to use the values in Table 3 of the right-hand branch of the curve seems justified.

On the basis of these considerations, it is possible to obtain a qualitative understanding of Equation (6). Obviously the rate of flow is higher at higher loads, but there is only a rough proportionality, as the experiments showed, and as has been found with other materials[23]. The rate of flow decreases progressively with time, because the points of slight change in potential have already undergone flow and therefore are again eliminated. As already explained, at high elongations the number of flat potential waves decreases, and this leads to stiffening and, consequently, to a decrease in the rate of flow. In the same way as with the yield point, the rate of flow is largely influenced by the thermal micromovement of the chains in accordance with Equation (9), so the reciprocal of the yield point can be used to express the temperature dependence in Equation (6). Attention should once more be called to one particularly noteworthy result of this work, *viz.* that the constant c is the same at all temperatures and for all the materials studied.

Finally Figure 5 can now be explained. With lowering of the temperature the tensile strength increases at first because of a lessening of the micromovements until, when the temperature becomes low enough, the brittleness increases to such an extent that an extreme value of the tensile strength is reached, as is evident in Figure 5. In the case of chain molecules, the freezing temperature and the temperature where the material becomes brittle do not

coincide[24]. For this reason a displacement of the extreme temperature shown in Figure 5 to lower temperatures compared to those in Figure 4 is understandable. The increase in brittleness depends on the development of a single solid range, but these two properties do not show any satisfactory correlation. The optical turbidity (the milky coloration) is likewise an indication of the development of a heterogeneous structure. The points of rupture of molecular dimensions which at first appear in the range of the microfluid state are quickly healed by the migration which is still continuing, but which subsequently ceases at lower temperatures and, with the onset of brittleness, rupture takes place.

SUMMARY

A more extended investigation was made of the surprising flow phenomena which were found in an earlier study of rubber at low temperatures. The tensile apparatus was reconstructed so that a dead-weight load could be applied to the rubber test-specimen. Determinations of the dependence of the rate of flow on time of stressing, initial elongation, magnitude of the stress, and temperature showed that a simple law can be derived for expressing the flow phenomena. Yield point, change in color, and deterioration in physical properties, as well as the reversibility of these phenomena were investigated and are discussed. The phenomena of flow at room temperature are expressed by the same constants as at lower temperatures. Only the effective stress increases at low temperatures and only by this change does flow become perceptible.

Different types of rubber were compared, and all showed approximately the same value for the flow constant. The essential characteristics of the flow phenomenon can be explained, on a basis of the theory of highly elastic materials, by their microliquid state of aggregation. This applies to the high degree of dependence of the mechanical properties of rubber on the temperature.

ACKNOWLEDGMENT

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[5] See Figure 1 in the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*).
[6] The symbols chosen here conform to those in the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*). The index 0 refers therefore in every case to the initial state, the overscoring to the tensile measurements (in contrast to the balloon-bursting experiment in the earlier work).
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[8] Figure 16 in the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*).
[9] Späth, "Physik der mechanischen Werkstoffprüfung", Berlin, **1938.**
[10] Figure 17 in the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*).
[11] Figure 18 in the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*).

[12] In the third part of this investigation on the bursting of recording balloons (which will appear soon in the *Annalen der Meteorologie*), this apparent error is eliminated by the introduction of a finite time of application of the stress, which was proved to be proportional to a. From the duration σ of the application of the stress, there is obtained, in place of Equation (4) for $t \gg \sigma$, Equation (5) as follows:

$$E = a \left(\ln \frac{t}{\sigma} + 0.577 \right)$$

$$0.577 - \ln \sigma \approx -1 = -\ln e$$

$$E = a \cdot \ln \frac{t}{e} + E_0 \; (t \text{ in seconds}; \; e = 2.718)$$

The differential form of Equation (5) on the contrary remains the same.

[13] The measurements shown in Table 14 of the earlier work (Rössler, *Abh. Marineobservat.* **8** (1944); subsequently published in *Ann. Meteorologie*) were not in this case utilized, since they were not obtained under conditions of constant load (weight). No dependence on time is involved because all values refer to 300 seconds.

[14] Houwink, "Chemie und Technologie der Kunststoffe", Leipzig, **1939**, p. 168, Figure 74.

[15] Scheele, Alfeis and Lahaye, *Kolloid-Z.* **103**, 1 (1943); **105**, 209 (1943).

[16] The author wishes to show his appreciation to Dr. Bächle, Leverkusen, for his preparation of thin films of these materials.

[17] Rössler, *Abh. Marineobservat.* **8**, 14 (1944); subsequently published in *Ann. Meteorologie*. The breaking elongation in this case also of about 7 as the lowest value may perhaps mean that the material had been overworked and, therefore, that its high breaking elongation dropped quickly to this value whenever it was overstressed.

[18] Müller, in Houwink, "Chemie und Technologie der Kunststoffe", Leipzig, **1939**; *Kolloid-Z.* **102**, 272 (1943).

[19] Ueberreiter, *Kolloid-Z.* **102**, 272 (1943).

[20] The difference between the coil theory (*cf.* Kuhn, *Kolloid-Z.* **76**, 258 (1936); *Angew. Chem.* **49**, 858 (1936); **51**, 640 (1938)) and the filament theory (*cf.* Bunn, *Proc. Roy. Soc.* (London) **180A**, 82 (1942)) in this respect is only mentioned at this time, with no attempt to discuss the subject in detail.

[21] Memmler, "Handbuch der Kautschukwissenschaften", Leipzig, **1930**.

[22] The temperature of stiffening, defined in this way as the minimum yield point, does not lie at −43° C (see Figure 4) but at −50° C (see Figure 6), and indicates only statistically the entire transformation interval. According to Ueberreiter (*Kolloid-Z.* **102**, 272 (1943)), the freezing temperature as defined on the basis of volumetric measurements appears to agree with the temperature according to Figure 6.

[23] Houwink, "Chemie und Technologie der Kunststoffe", Leipzig, **1939**, p. 163, Figure 71.

[24] Scheele, Alfeis, and Friedrich, *Kolloid-Z.* **108**, 45 (1944), which contains further references.

DETERMINATION OF THE MOLECULAR WEIGHT OF RUBBER AND POLYSTYRENE BY THE METHODS OF LIGHT SCATTERING AND OSMOMETRY *

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One of the newest methods of investigation of high-polymeric substances is the determination of their molecular weights from the light scattering of their solutions. The method is based on the measurement of the intensity of light scattered by the solution, since this intensity is related in a definite manner to the particle size of the dissolved substance. To make possible exact measurements, the light-scattering intensity must be sufficiently high (of the order of 10^{-3}–10^{-4} cm.); *i.e.*, the particles of the dissolved substance must be large. However, the particle size of the dissolved substance must not exceed one-tenth of the wave length of the light employed to illuminate the solution. If the particle size becomes comparable with the wave length, the measured light scattering can no longer be correlated in any simple way with the size of the particles causing this scattering.

Solutions of high-polymeric substances are precisely the type of solutions satisfying the above requirements. It is true that, in the majority of high-polymeric substances, the chain length frequently exceeds the wave lengths in the visible spectrum. But, because of their flexibility, chain molecules exist in solution in the form of arbitrarily tangled coils, the external dimensions of which are considerably smaller than the wave length of light.

The theory of light scattering by liquids was developed by Einstein and Smoluchowski[1]. Debye was the first to apply this theory to the determination of the molecular weights of high-polymeric substances[2]. The method of light scattering was successfully employed by Debye[3] for determining the molecular weights of polystyrene and polyvinyl esters, and by other investigators[4] for determining the molecular weights of polystyrene and cellulose acetate.

Great interest attaches to the introduction of this method into our Soviet research practice, and to the extension of the field of application of the method by applying it to various rubbers, which occupy one of the most important places among the technically significant high-polymeric substances.

The theory of light scattering by pure liquids and solutions was developed by Einstein and Smoluchowski on the basis of their concepts of the optical heterogeneity of a liquid resulting from thermal fluctuations of density and concentration[1]. The end result of Einstein's thermodynamic computations may be represented by the following formula:

$$\tau = \frac{32\Pi^3}{3} \cdot \frac{n_0^2}{N_0\lambda^4} \cdot c \frac{(c\partial n/\partial c)^2}{\partial(p/RT)/\partial c} \qquad (1)$$

* Translated for Rubber Chemistry and Technology from the *Kolloidnĭ Zhurnal*, Vol. 11, No. 3, pages 143–150 (1949), by Alexander Bugrow, Cambridge, Massachusetts.

where τ is the turbidity of the solution in cm.$^{-1}$; n_0 is the index of refraction of the solvent; N_0 is Avogadro's number; λ is the wave length in cm.; c is the concentration in grams per cc.; $\partial n/\partial c$ is the concentration gradient of the index of refraction; and $\partial(p/RT)/\partial c$ is the concentration gradient of the osmotic pressure.

In Equation (1), the light-scattering intensity of the solution is connected with the change in the index of refraction during the transition from the solvent to the solution. The inverse correlation between the turbidity and the concentration gradient of the osmotic pressure expresses Einstein's fundamental proposition in connecting the extent of fluctuations with the free energy change accompanying these fluctuations. The fluctuations are the smaller, the higher the osmotic pressure required to produce a local change in concentration.

Designating the constants entering into Equation (1) by H, we obtain:

$$\tau = H \frac{c}{\frac{\partial(p/RT)}{\partial c}} \quad \text{or} \quad Hc/\tau = \frac{\partial(p/RT)}{\partial c} \tag{2}$$

where:

$$H = \frac{32\Pi^3}{3} \frac{n_0^2}{N_0\lambda^4} \left(\frac{\partial n}{\partial c}\right)^2$$

The osmotic pressure of dilute solutions of high-polymeric substances may be expressed by the following empirical equation:

$$\frac{p}{RT} = \frac{c}{M} + Bc^2 \tag{3}$$

where B is a constant determined by the solvent-solute system, and M is the molecular weight of the dissolved substance.

By substitution and differentiation, we obtain:

$$H\frac{c}{\tau} = \frac{1}{M} + 2Bc \tag{4}$$

The same results were obtained by Debye on the basis of an independent direct computation of the field of a particle excited by light impinging upon it. Such a computation is possible for the region of extremely dilute solutions with small particles, which are considered as isolated dipoles vibrating with the frequency of light. In the direct method of computing the light-scattering intensity, the demonstration of the independence of the end result from the shape of the particles is of great value, since no limitations of any kind are imposed upon the particle shape during the computation.

In the expression for H, the concentration gradient of the index of refraction, $\partial n/\partial c$, may be replaced by the ratio $(n - n_0)/c$, where n is the index of refraction of a solution of the concentration c. Such a substitution is possible because of the fact that, in the range of dilutions usually studied, the difference $(n - n_0)$ is strictly proportional to the concentration.

It follows from Equation (4) that the value of $H\frac{c}{\tau}$ is a linear function of the concentration. The ordinate segment cut off by the straight line plotted on the coördinates $H\frac{c}{\tau}$ against c equals the reciprocal of the molecular weight. Thus, to determine a molecular weight from light scattering, it is necessary to

measure the indices of refraction of the solvent and solution at some one concentration and light-scattering intensity for several concentration levels. From this the limiting value of $H\frac{c}{\tau}$ at $c \to 0$ is graphically determined, which, as already indicated above, equals the reciprocal of the molecular weight. For a polydisperse solution, the ordinate segment equals the reciprocal of the weight average of the molecular weights.

As already pointed out, the formulas above apply to the case of particles that are very small in comparison with one wave length. As the size of the particles increases and approaches the order of a wave length, the phase lag of the waves radiated by individual portions of such a microparticle increases correspondingly. As a result of interference of waves that differ in phase, the angular distribution of the intensity of the scattered light changes. For small angles of observation, the intensity remains practically the same as if the dissolved substance were dispersed as small particles; as the angle of observation increases, a lower intensity of the light-scattering is observed. Debye proposed the computation of a correction based on a comparison between the actual angular distribution and the distribution of small particles, which is proportional to $(1 + \cos^2 \vartheta)$, where ϑ is the angle between the direction of the incident light and the direction of observation. Instead of comparing each time the measured intensity with that derived by computation, a coefficient of dissymmetry is determined by comparing the scattering intensities at two angles symmetrical with respect to 90°, for example 51° and 129°. Then a curve correlating the correction factor with the coefficient of dissymmetry is plotted.

It should be pointed out that the determination of the angular distribution of light scattering provides a broad characterization of the state of the molecules in the solution, and supplements the data on their molecular weight by information on the external dimensions of the molecules. In the work of Doty, an attempt was made to calculate the linear dimensions of cellulose acetate molecules in acetone, and it was established that maximum extension is associated with moderate molecular weights, since the asymmetry of angular distribution undergoes almost no increase as the molecular weight increases[4]. The relatively small increase in the external dimensions of the molecule with increasing molecular weight may be explained by the flexibility of the molecule, as a result of which long molecules coil up and their external dimensions become greatly reduced. Generally speaking, the asymmetry of the angular distribution of light scattering is not great. The maximum corrections constitute 8–12 per cent of the measured turbidity. This confirms the correctness of modern concepts relative to the shape of polymeric molecules in dilute solutions, this shape being visualized as that of a tangled coil.

The last factor which should be noted during this brief discussion of the theory of the method is the absence of depolarization corrections in Equation (4). Debye indicates that his measurements led to a correction affecting the molecular weight by less than 2 per cent, *i.e.*, within the range of errors in measuring the turbidity[3].

The work of Frisman and Tsvetkov is highly convincing, for they demonstrated the insignificant degree of depolarization connected with the optical anisotropy of molecules of rubberlike substances[5]. The geometric anisotropy of polystyrene and polymethyl methacrylate is not reflected at all in the depolarization effect. The authors note that, apparently, "in the process of light scattering, the part of the active unit is played by the macromolecule of the polymer as a whole, and not by the monomeric link of the chain, as is the

case, for example in the phenomena of dielectric polarization or of the magnetic birefringence of the solution". The only case in which the depolarization effect manifested itself was observed by Frisman and Tsvetkov in solutions of Oppanol in carbon tetrachloride; this effect, however, was caused by the size of the particles and not by their anisotropy, since the increase in the depolarization factor was noted only with horizontally polarized light, indicating a dependence on the size of the light-scattering particle. In measurements of the intensity of light scattering, this Oppanol solution should have shown an asymmetric angular distribution of light scattering. Thus, the absence of depolarization corrections in the formulas proposed for computations is fully justified.

EXPERIMENTAL PART

Determination of molecular weight from light scattering.—In the present work the indices of refraction of the solutions and solvents were measured by means of a Pulfrich refractometer. The determinations were carried out with the green line of a mercury lamp. The concentration gradient of the index of refraction was determined by means of measurements of the index of refraction of solutions containing 0.8–1.2 grams of solute per 100 cc. The light scattering of solutions was measured with a Leitz nephelometer at a 90° angle of observation. The light source was a PRK-4 mercury lamp, provided with a light filter transmitting only the green line of the mercury spectrum, $\lambda = 546$ mμ. As a standard turbidity, a turbid glass column calibrated for its absolute turbidity on the basis of a Zeiss prism of known turbidity was employed. Since the turbidity of the majority of solutions investigated was considerably lower than that of the glass column intermediate standard solutions of gelatin in water were prepared. The precision of the turbidity measurements at an absolute value of 10^{-3} cm.$^{-1}$ constituted 2.5 per cent. The layout of the nephelometric apparatus is represented in Figure 1.

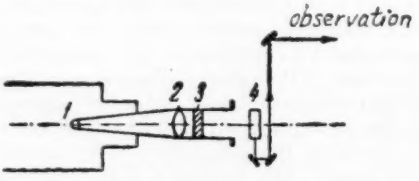

FIG. 1.—Schematic diagram of nephelometer. 1—Mercury lamp. 2—Lens. 3—Light filter. 4—Test cell.

The molecular weights of four fractions of different samples of polymethyl methacrylate, unfractionated polystyrene, butadiene-styrene rubber, two types of natural rubber, and brominated rubber were determined by the method of light scattering.

The solvents were dried thoroughly and were purified by repeated distillations. The solutions of high-polymeric substances were purified by reprecipitation and filtration through glass filters of medium density. The natural and butadiene-styrene rubbers were extracted with cold acetone before precipitation. In the case of natural rubber, all operations were conducted in purified nitrogen, which was freed from traces of oxygen and moisture by passage at 300° C over copper deposited on silica gel, followed by drying in a train consisting of sulfuric acid, calcium chloride, and phosphorus pentoxide.

TABLE 1

MOLECULAR WEIGHT OF RUBBERS AND POLYSTYRENE

Name of substance	Solvent	Molecular weight: Light-scattering method	Molecular weight: Osmometric method	Molecular weight: Viscosimetric method
Polystyrene I (thermal polymer)	Benzene	385,000		
Polystyrene II (prepared with initiator)	Benzene	200,000		
Polymethyl methacrylate (fractionated) I	Acetone	417,000		
Same, II	Acetone	588,000		
Same, III	Acetone	625,000		
Same, IV	Acetone	2,000,000		
Butadiene-styrene rubber (sol fraction)	Toluene	200,000	96,000	
Butadiene-styrene rubber (technical)	Benzene		370,000	440,000
Brominated rubber (pale crepe)	Chloroform	400,000		
Natural rubber (smoked sheet)	Toluene* †	200,000–280,000	200,000–240,000	178,000–200,000
Natural rubber (pale crepe, middle fraction)	Toluene* †	215,000–270,000	220,000	200,000

* In Experiments 9 and 10, 5 per cent of methanol was added to the solvent for the determination by the light-scattering method only.

† Two values for molecular weights in Experiments 9 and 10 correspond to extreme values obtained with different solutions prepared from the same original rubber sample.

TABLE 2

MOLECULAR WEIGHT OF RUBBER DETERMINED BY DIFFERENT METHODS

Substance	Method	Molecular weight	Author
Natural rubber	Osmometric	200,000–240,000	Present work
Natural rubber in ether (sol rubber)	Ultracentrifuge	400,000–435,000	Kraemer[8]
Natural rubber in CCl_4	Diffusion	400,000	Pasynskii and Gatovskaya[9]
Natural rubber in toluene* 5% alcohol	Light scattering	200,000–280,000	Present work

The results of the molecular-weight determinations are presented in Table 1. Figures 2 and 3 show graphical determinations of $\left(H\frac{c}{\tau}\right)_{c\to 0}$ for some of the preparations.

Determination of molecular weight from viscosity and osmotic pressure.— Viscosity was measured in an Ubbelohde viscometer for volatile liquids. The molecular weight was calculated by the following formula:

$$[\eta] = KM^a$$

where η is the characteristic viscosity, M is the molecular weight, and K and a are constants.

For natural rubber, K was assumed to equal $1.4\cdot 10^{-4}$; $a = 1$[6]. Concentration was expressed in moles per liter. For butadiene-styrene rubber, $K = 5.4\cdot 10^{-4}$; $a = 0.66$[7]. Concentration was expressed in grams per 100 cc.

In the osmometric measurement of the molecular weight, a glass osmometer of the type proposed by Dogadkin for the measurement of osmotic pressure by a statistical method was employed; this instrument has been employed rather widely during the past two years.

The osmometer (Figure 4) consists of a glass cell 1 with a capacity of about 15 cc. The lower edge of the cell is about 3.5 cm. in diameter. The bottom of the cell consists of a semipermeable membrane, which is glued to the ground edge 2 of the cell. The solution is poured into the cell through the side arm 3, which is closed with a ground-glass plug 4. A hermetic closure is obtained with the aid of the mercury seal 8. (In the case of solvents such as benzene, a dextrin lubricant is used.) The upper part of the cell terminates in the graduated capillary 5, 0.7 mm. in diameter and 12–15 cm. long; another, exactly similar, capillary 6, attached to the first in such a manner that its end is immersed in the solvent bath, serves to measure capillarity. The cell is placed on the ground ring 7, located on the bottom of the vessel containing the solvent. The vessel is closed with ground-glass cap 9.

The experiments were conducted with membranes designated as "Ultra-Cella-Filter, Fine", with which equilibrium was attained 4–6 hours after the start of the experiment. The membranes were treated with alcohol, and were

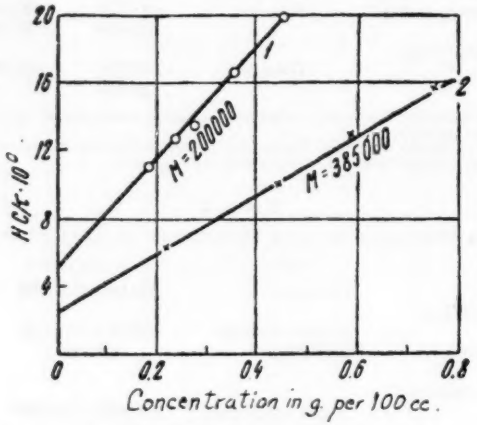

FIG. 2.—Molecular-weight determination by the light scattering method. 1—Butadiene-styrene copolymer. 2—Polystyrene.

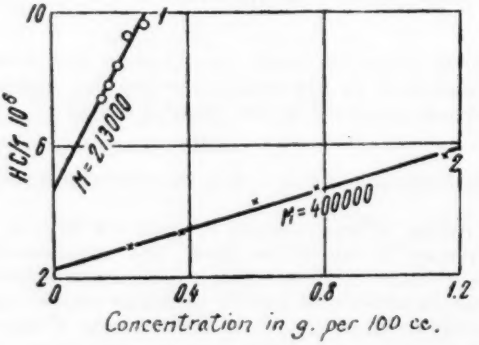

FIG. 3.—Molecular-weight determination by the light scattering method. 1—Natural rubber. 2—Brominated natural rubber.

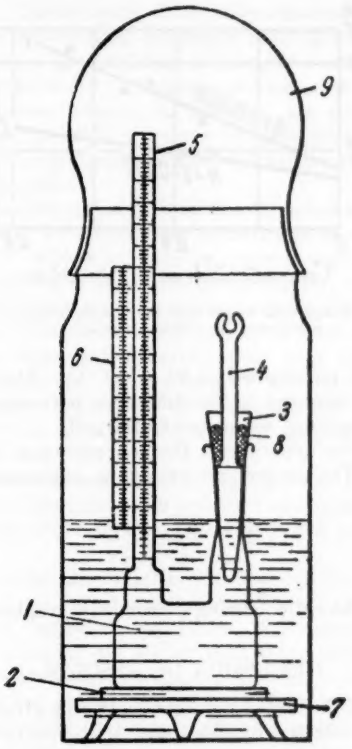

FIG. 4.—Diagrammatic sketch of the osmometer (it is described in the text).

glued on with an aqueous solution of polyvinyl alcohol. The adhesive film was then heated for 20 minutes at 70–100° C, the membrane being held close to the cell by a small weight. After being glued on in this manner, the membrane was washed with the solvent, and was kept in the latter all the time until the experiment was started.

More recently, we have been using collodion membranes prepared by the method of Montonna and Jilk[10]. The membrane is glued not only to the edge of the cell but also to the ring, which is held close to the cell by means of a weight during the gluing operation. In this manner, the membrane becomes very firmly attached, and the osmometer can be used with a single membrane for several months of uninterrupted work.

Before filling the osmometer, the temperature of the solution and solvent is adjusted to 25° C. The solution is poured into the cell, and its level is adjusted as desired by moving the plug and slightly inclining the cell. Any excess of the solution is pressed out above the ground-glass portion of the plug as the latter is inserted. Mercury is introduced into the seal, and the excess solution above the level of the mercury is removed with filter paper. The cell is placed carefully, so as not to damage the membrane, on the ring in the vessel, which is already filled with solvent. The level of the latter is adjusted to the lower level of the mercury in the side arm. The vessel with the cell is immersed

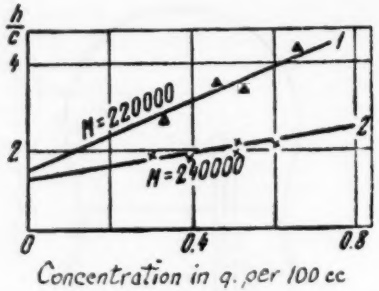

FIG. 5.—Determination of molecular weight from the osmotic pressure. 1—Middle fraction of pale crepe. 2—Smoked-sheet rubber.

in a water thermostat maintained at $25 \pm 0.1°$ C. The height to which the solution rose (h) was recorded as the difference between levels in the control capillary and in the capillary connected to the cell.

On completion of the experiment, the concentration of the solution in the cell is determined. The molecular weight is calculated by the following equation:

$$M = \frac{RT}{\delta} : \lim_{c \to 0} \frac{h}{c}$$

the limiting value of the ratio $\frac{h}{c}$ being determined graphically (Figure 5).

DISCUSSION OF RESULTS

As indicated above, the method of light scattering gives the average molecular weight, and is not affected by the shape of the particles. In consequence of this, the method of light scattering is, in some cases, the only method applicable. A notable advantage of the method is also that it makes possible operations in the region of high dilutions, and the higher the molecular weight the lower may be the concentration of the solutions studied.

On the other hand this method has some fundamental limitations, and involves a number of experimental difficulties. The former include primarily the limitation which must be imposed upon the size of the particles studied. The necessity of introducing corrections when particles comparable with a wave length are present increases the possibility of errors. In certain cases, as, for example, with solutions of natural rubber, it is possible to avoid the necessity of applying corrections by the proper choice of solvent. The configuration of molecules in solution depends on the solvent. Apparently, in "good" solvents, the flexible molecules of high polymers are more loosely coiled, as a result of which their volume is larger. This procedure, however, should be used very cautiously, since the shrinkage of individual molecules in "poor" solvents is always accompanied by the formation of aggregations, and in some cases such aggregations remain intact, even in very high dilutions. The latter circumstance may lead to a determination of the particle weight, and not of the molecular weight, even on extrapolation to infinite dilution (natural rubber in halogenated solvents).

Among the experimental difficulties must be included the inevitable existence of a sufficiently large difference between the refractive indices of the

solution and solvent. On the basis of the determinations in the present work, as well as of the data reported by American investigators, it has been established that the difference in refractive indices for 1 per cent solutions must amount to about 0.0005–0.001. Because of this, many generally accepted solvents, such as benzene, toluene, or naphtha, are not suitable for natural rubber. In some cases, the difficulties can be eliminated by the use of binary solvents; this, however, is undesirable, since the execution of the measurements is then greatly complicated.

Other experimental difficulties include the exceptionally high purity of the test solutions required. Low-molecular admixtures in amounts incapable of changing the index of refraction have no serious significance. Mechanical contaminants are easily removable and, consequently, do not complicate the operation. The most serious obstacle is the presence of high-molecular admixtures, since their removal is always difficult, while even in insignificant quantities in the solution under investigation, they may completely distort the results of the determinations. In the case of colored solutions, it is nearly always possible to select a primary color outside the absorption spectrum. However, the necessity of investigating a broad spectral region in such cases is an added difficulty.

The above-mentioned experimental difficulties are not fundamental, and the relative simplicity of the apparatus and the rapidity of obtaining the results have made the wide use of the method desirable in the practice of our research work.

In comparing the molecular weights obtained by the authors with the aid of the methods of light scattering and osmometry, note should be made of the satisfactory agreement between the results. In isolated cases, the values obtained from light scattering are higher than those obtained by osmometry; this is quite natural in the case of polydisperse systems, since the light-scattering method yields a weighted average molecular weight, whereas the osmometric method yields an arithmetic average molecular weight. The data on the molecular weight of natural rubber obtained both by the method of light scattering and by the method of osmometry agree with previously reported values (see Table 2). The discrepancies do not exceed those expected of different preparations.

CONCLUSIONS

1. Experiments on the determination of the molecular weights of natural rubber and other high-molecular compounds by the methods of light scattering and osmometry are reported.

2. An osmometer of new design, suitable for determining molecular weights, is described.

3. It is shown that the method of light scattering yields values for molecular weights which are in satisfactory agreement with those obtained by the method of osmometry.

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INFRARED STUDIES OF 1,2- AND TRANS 1,4-STRUCTURE OF POLYBUTADIENE AND BUTADIENE-STYRENE COPOLYMERS POLYMERIZED AT VARIOUS TEMPERATURES *

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One of the major improvements in the quality of synthetic butadiene rubbers has resulted from the use of low temperatures of polymerization. In particular, tensile strength, resilience, flex life, abrasion resistance and processing properties of tire-tread stocks have been favorably affected[1].

It is of great importance to determine the reasons for improvements in the physical properties of low temperature polymers to expedite future research. Comparison of the physical properties of Hevea rubber with isomerized rubber or synthetic polyisoprene illustrates the point that crystallizable polymers are required for high tensile strengths, particularly in gum vulcanizates. From the low tensile strengths obtained on isomerized rubber it may be concluded that the existence of random sequence of *cis-trans* configurations is sufficient to prevent crystallization during stretching of the rubber. Also in synthetic polyisoprene, polybutadiene and GR-S, appreciable quantities of 1,2-addition are found and become the source of further irregularities in the chain structure of the polymer. 1,2- and *cis-trans* 1,4-additions in random sequence may be considered as the major structural variations leading to noncrystallizable and inferior polymers. To determine the relative importance of 1,2- and *cis-trans* 1,4-addition, it is necessary to develop analytical methods for these isomeric units present in butadiene polymers.

Several methods have been employed in the determination of the amount of 1,2-addition in polybutadiene and butadiene-styrene copolymers. In emulsion polymers it has been reported that 78 per cent of the butadiene addition is in the 1,4-configuration and the remainder in the 1,2-configuration[2]. Therefore 78 per cent of the butadiene is present as *cis-trans* isomers of the 1,4-addition product arranged in random sequence. From the results on isomerized rubber it would be expected that, even if the 1,2-addition could be reduced to negligible values, inferior products would still result because of the presence of the large amount of *cis-trans* isomers in random sequence.

Beu, Reynolds, Fryling and Murry[3] reported that crystallization can be developed in polybutadiene prepared at 20° and lower. Further, they deduced from their *x*-ray work that the partially crystallized rubber corresponded to the *trans*-configuration. However, it is difficult to measure the *trans*-isomeric content of the polymer quantitatively or even relatively by *x*-ray methods. Ozonization[4], perbenzoic acid[5], and infrared[6] methods have been applied to the

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measurement of the percentage 1,2-addition in butadiene polymers. Of these methods the perbenzoic acid and infrared methods are in fair agreement.

The present paper shows that the infrared spectrometer is admirably suited not only to the measurement of 1,2-addition but also to the measurement of *trans*-1,4-addition in polybutadiene and butadiene-styrene copolymers. It is the purpose of this paper to describe briefly the 1,2- and *trans*-1,4-addition analytical methods and also to report results on the effect of temperature of polymerization and styrene content on 1,2- and *trans*-1,4-addition in butadiene polymerization and copolymerization.

EXPERIMENTAL

Materials.—The emulsion polymers used in this study are listed in Table I. These were secured from the following sources; the 14R and 26E series[7] were obtained from the Synthetic Rubber Laboratories, University of Akron; the J888–J949 series was obtained from the Synthetic Rubber Division, United States Rubber Company, Naugatuck, Connecticut; GR-S and GR-S10 were regular commercial materials.

TABLE I

ANALYTICAL DATA ON POLYBUTADIENE AND BUTADIENE-STYRENE COPOLYMERS

Polymer code[a]	Pol. temp. (° C)	B/S charge ratio	n_D^{25}	% comb.[d] styrene	η_0 (CS_2)	% 1,2[b]	% 1,2 (cor.)	% *trans*.[b]	% *trans*. (cor.)	1,4/1,2	Ratio *trans* −*cis*
14R5	+97	100/0	1.5159	0.74	Gel	21.0	24.8[c]	51.4		3.03	2.16
14R6	+65	100/0	1.5156	0.37	Gel	22.1	23.8[c]	56.6		3.20	2.89
14R3	+50	100/0	1.5156	0.37	2.15	23.2		62.0		3.31	4.2
26E77–96	+ 5.5	100/0	1.5154	0.13	1.96	21.0		72.0		3.70	10.3
26E77–96	+ 5.5	100/0				21.6		71.4			
J946–4	+ 5	100/0	1.5148	−0.60	2.80	20.8	20.8	71.5		3.80	9.3
26E25–40	−10	100/0				19.8		74.8		4.05	13.9
26E41–56	−10	100/0	1.5144	−1.09	2.81	20.6		76.3		3.85	24.6
26E57–76	−19	100/0	1.5143	−1.22	1.02	19.6		79.6		4.10	100
J947–2	+ 5	95/5	....	3.8	2.60	20.2	21.0	68.6	71.3		
J948–B2	+ 5	90/10	1.5219	7.6	1.98	17.9	19.4	67.1	72.7		
J949–4	+ 5	85/15	....	12.7	1.72	18.4	20.9	64.9	73.8		
J888–3	+ 5	71/29	1.5344	23.3	2.11	16.1	21.0	58.3	76.1		
J889–3	−18	71/29	1.5352	24.3	3.16	14.8	19.6	63.5	83.9		
GR-S	+50	71/29	1.5345	23.4	2.08	16.8	21.9	49.6	64.8		
GR-S10	+50	71/29	1.5331	21.8	Gel	15.7		45.4			

[a] The 14R and 26E series of polymers were obtained from the Government Laboratories, Univ. of Akron, and the J series was obtained from the U. S. Rubber Company, Synthetic Rubber Division, Naugatuck, Connecticut. 14R3, 14R5, 14R6, GR-S 10 and GR-S are made with persulfate formulas; the remainder of polymers are made with cumene hydroperoxide-Redox formulas. [b] An additional correction of −0.03X% styrene should be made for the absorption of combined styrene present in the copolymer. This is due to absorption of styrene at 910 and 967 cm.$^{-1}$. [c] See dotted line of Figure 4. [d] Based on refractive index measurements and equations of Madorsky and Wood[12]. Actual % styrene in polybutadiene is zero.

Purification of polymers.—Since it is desirable to use carbon disulfide solutions of the polymers for the infrared analysis, the following purification method was used: 2 grams of the polymer was dissolved in 100 cc. of carbon disulfide, and the solution was filtered through 300-mesh silk gauze to remove gel. Methanol was added to the filtered solution until complete precipitation took place. The precipitated polymer was then evaporated to dryness at room temperature. During this evaporation process two or three additions of carbon disulfide were made to facilitate removal of methanol from the polymer.

Preparation of solutions.—The polymer purified as described above and freed from methanol was dissolved in carbon disulfide and made up to concen-

trations of 3 to 4 per cent. Care was necessary in the purification process to minimize the danger of gelation by keeping the temperatures and exposure to air as low as possible. 14R5, 14R6 and GR-S10 were not obtained gel-free, and these polymers were analyzed in the partially gelled condition.

Spectroscopic methods.—A Perkin-Elmer spectrometer was used for infrared studies of polymer structure[8]. Details of the procedure will be described in a separate paper. Measurements of the intensities of absorption were made in the 900–1000 cm.$^{-1}$ region using solutions of the polymer in carbon disulfide.

For measurement of 1,2-addition in butadiene polymers the absorption of the 910 cm.$^{-1}$ infrared band by the polymer solution was compared with the absorption by octene-1 of National Bureau of Standards grade.

Absorption of the 967 cm.$^{-1}$ infrared band was used to measure the percentage *trans*-1,4-addition in butadiene polymers. *trans*-4-Octene obtained from the National Bureau of Standards was employed for calibration purposes.

A study[9] of the National Bureau of Standards Spectra[10] of *cis*-2-butene, *trans*-2-butene, *cis*-2-pentene and *trans*-2-pentene reveals the fact that the 967 cm.$^{-1}$ band is more strongly absorbed by the *trans*-isomers than by the *cis*-isomers. Figure 1 contains N.B.S. spectra of *cis*-2-pentene and *trans*-2-pentene and our measurement of *trans*-4-octene. In Figure 2 our measurements of the

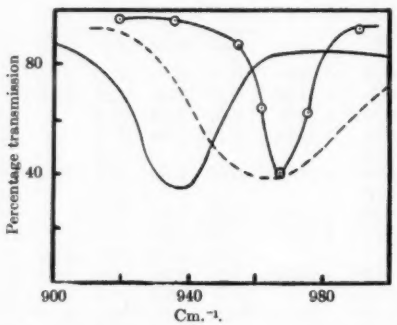

FIG. 1.—Infrared transmission curves for *cis*- and *trans*-2-pentene and *trans*-4-octene: —, *cis*-2-pentene, 10-cm. cell, 100 mm.; - - -, *trans*-2-pentene, 10-cm. cell, 39 mm.; O, *trans*-4-octene, CS_2, 30.15 g./l., 0.01045 cm. Curves for *cis*-2-pentene and *trans*-2-pentene determined from National Bureau of Standards Spectra 357 and 358, respectively, American Petroleum Institute Project 44.

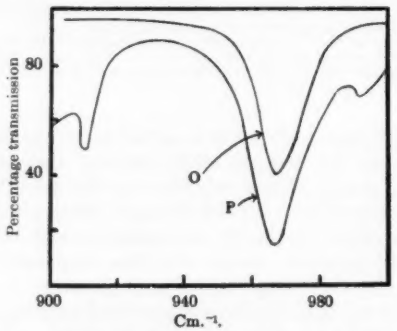

FIG. 2.—Infrared transmission curves for *trans*-4-octene and polybutadiene, cell length 0.01045 cm., CS_2 solvent: O, *trans*-4-octene, 30.15 g./liter; P, polybutadiene 26E77–96, 36.82 g./liter.

spectra of *trans*-4-octene and polybutadiene are shown to have absorption peaks at 967 cm.$^{-1}$. Therefore, it is concluded that the 967 cm.$^{-1}$ band may be used to measure *trans*-1,4-addition in butadiene polymers.

Calibration.—The calibration curves are given in Figure 3. The molar extinction coefficient of octene-1 is 155. The same value was used for the vinyl side-group resulting from 1,2-addition in polybutadiene.

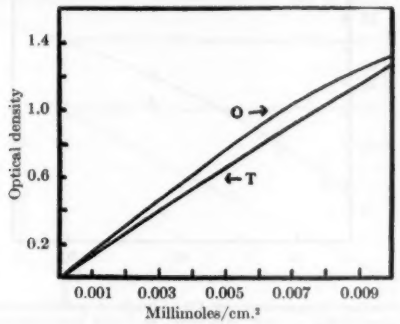

FIG. 3.—Calibration curves for 1,2- and *trans*-1,4-addition in butadiene polymers: O, 1,2-addition based on 1-octene; T. *trans*-1,4- based on *trans*-4-octene.

Molar extinction coefficients of the 967 cm.$^{-1}$ band were determined for three *trans*-olefins. These results appear in the following table.

Olefin	Molar extinction coefficient ϵ
trans-4-Octene	132 ± 2
trans-3-Hexene	133 ± 2
trans-2-Hexene	157 ± 2

where $\epsilon = \log (I_0/I_t)/cd$.
c = concentration in moles/liter.
d = thickness of solution in cm.
I_0, I_t = initial and transmitted light intensity, resp.

Here it is shown that *trans*-3-hexene and *trans*-4-octene have practically identical extinction coefficients, whereas that of *trans*-2-hexene is somewhat higher. There is a possibility that the absorption by the *trans*-1,4-unit in butadiene polymers would be affected by adjacent styrene or 1,2-addition structures. Since these structures are present in relatively small amounts, they are considered to have a secondary influence. Hence we assume that the molar extinction coefficients of the 967 cm.$^{-1}$ bands of the *trans*-4-octene and the *trans*-1,4-unit in butadiene polymers are identical. The *trans*-1,4-calibration curve in Figure 3 is based on this assumption.

RESULTS AND DISCUSSION

From the optical density of the band, concentration of polymer solution and thickness of the absorption cell, the percentage 1,2- and *trans*-1,4-addition were calculated. Experimental results are given in Table I for butadiene-styrene copolymers and for polybutadiene polymerized at temperatures ranging from −19 to +97°.

Effect of temperature of polymerization on 1,2-addition.—In Table I and Figure 4 it is shown that the temperature of polymerization has a relatively

small effect on 1,2-addition for polybutadiene and butadiene 71-styrene 29 copolymers. A maximum of 23.2 per cent 1,2-addition exists at 50°, which is in excellent agreement with the 23 per cent found by Kolthoff, Lee and Mairs[11]. The amount of 1,2-addition decreases continuously with polymerization temperature to a value of 19.6 per cent at −19°.

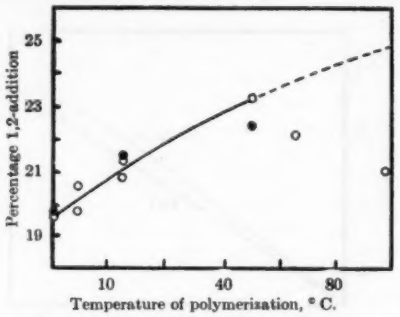

FIG. 4.—Effect of polymerization temperature on 1,2-addition in polybutadiene and 71/29 butadiene-styrene copolymers: ○, polybutadiene; ●, 71/29 butadiene-styrene.

With reference to the polymers prepared at 65 and 97°, the spectra were run on samples that had partially gelled. The apparent decrease in 1,2-addition for these 65 and 97° polymers as the temperature is raised above 50° is interpreted as branching or cross-linking reactions that selectively attack the vinyl side-groups in polybutadiene. If we assume that 1,2-addition follows the dotted line in Figure 4, for temperatures of polymerization beyond 50°, then 3.8 and 1.2 per cent of the 1,2-addition product have reacted at polymerization temperatures of 97 and 65°, respectively. Further work on polymers prepared at temperatures above 50° is in progress to clear up this point.

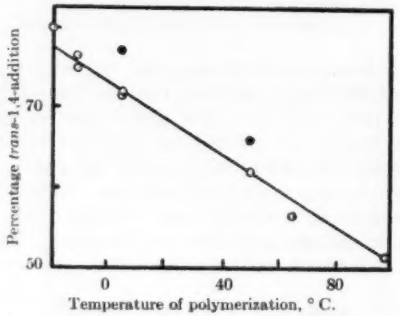

FIG. 5.—Effect of temperature of polymerization on *trans*-1,4-addition in polybutadiene and 71/29 butadiene-styrene copolymers: ○, polybutadiene; ●, 71/29 butadiene-styrene copolymers.

A reduction in temperature of polymerization from 50 to −19° results in only a 3.6 per cent decrease in percent 1,2-addition. This small change in percentage 1,2-addition could hardly be expected to account for the considerable improvement in crystallization and physical properties of butadiene polymers prepared at low temperatures.

Effect of temperature of polymerization on trans-1,4-addition.—The *trans*-1,4-content of polybutadiene and 71/29 butadiene-styrene copolymers is given in Table I and shown in Figure 5. It is found that *trans*-1,4-increases continuously from a value of 51.4 per cent for the 97° polymer to 79.6 per cent for the −19° polymer. This is a change of 28.2 per cent and is considerably greater than the change of 3.6 per cent found in 1,2-addition. Furthermore, the results indicate that at −19° substantially all of the 1,4-addition product is in the *trans*-form.

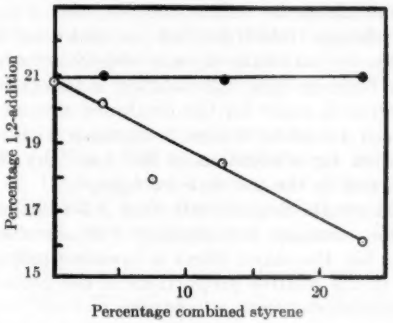

FIG. 6.—Effect of styrene on 1,2-addition in butadiene-styrene copolymers prepared at 5°: ○, uncorrected; ●, corrected for styrene content.

At 5° the ratio of *trans* to *cis* is 10.3, whereas at 50° it is 4.2. These changes should greatly enhance the ability of the polymer to crystallize on stretching, especially at low temperatures. This result has been demonstrated by the previously mentioned *x*-ray results[3].

Effect of combined styrene.—Figure 4 also shows that the percentage 1,2-addition in butadiene 71-styrene 29 copolymers decreases as the temperature of polymerization is lowered. A substantially identical decrease is observed for both polybutadiene and butadiene-styrene copolymers. The result indicates that the styrene unit has no influence in altering the ratios of 1,2- and 1,4-addition as polymerization temperatures are lowered. This is in agreement with the results of Kolthoff, Lee and Mairs[11], who employed the perbenzoic acid method for studying 1,2-addition.

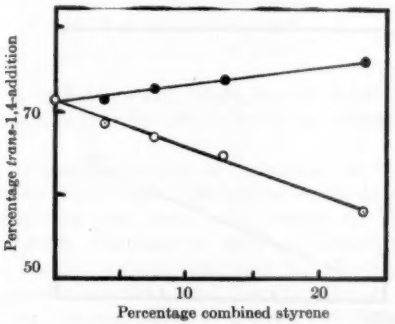

FIG. 7.—Effect of styrene on *trans*-1,4-addition in butadiene-styrene copolymers prepared at 5°: ○, uncorrected; ●, corrected for percentage of styrene.

In Figure 5, the percentage *trans*-1,4- in the butadiene 71-styrene 29 copolymers also is shown to increase with lowering of polymerization temperatures. The percentage *trans*-1,4- is greater than that for polybutadiene. The correction for absorption at 967 cm.$^{-1}$ by styrene residues is -0.03 per cent per per cent combined styrene. If this were applied to the values in Figure 5, it would be insufficient to account for the differences from polybutadiene. It is possible that the adjacent styrene residues have some effect on the molar extinction coefficient of *trans*-1,4-configurations, but suitable reference compounds are not now available for calibration purposes.

The influence of change from 0 to 23.3 per cent combined styrene on 1,2- and *trans*-1,4-addition in butadiene-styrene copolymerization at 5° is shown in Table I. Figure 6 shows that 1,2-addition is independent of the styrene content when correction is made for the combined styrene in the copolymers. In Figure 7 the *trans*-1,4-content is seen to increase with increasing combined styrene after correction for absorption at 967 cm.$^{-1}$ by the styrene residues. This effect was discussed in the previous paragraph.

The experimental results demonstrate that 1,2-addition decreases slightly and *trans*-1,4-addition increases considerably with decreasing temperature of polymerization. By far, the major effect of lowering polymerization temperature is this increase in the relative proportions of the *trans*-1,4-configuration in polybutadiene or butadiene-styrene copolymers.

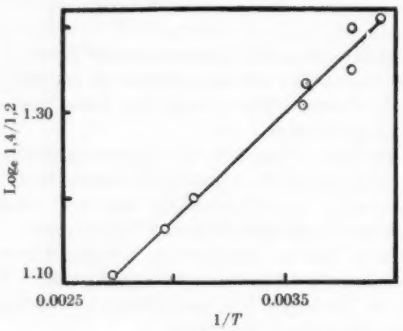

FIG. 8.—Log$_e$ of 1,4/1,2 *versus* $1/T$ in polybutadiene

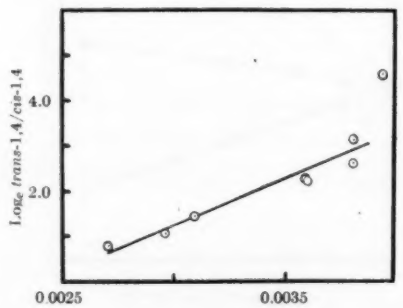

FIG. 9.—Log$_e$ *trans*-1,4/*cis*-1,4 *versus* $1/T$ in polybutadiene

Refractive index of polymers.—The refractive indices and intrinsic viscosities of the polymers used in these studies are given in Table I. The method used for refractive index is similar to that of Madorsky and Wood[12]. The refractive index of polybutadiene is shown to decrease with decreasing temperature of polymerization. Since the change is only about 0.3 per cent, no correction was made in combined styrene determinations by the refractive index method on butadiene-styrene copolymers prepared at low temperatures.

Free energy, heat and entropy of activation.—Since the 1,2-addition and *trans*-1,4-addition are known in these purified polymers, it is possible to estimate the percentage *cis*-1,4-addition. One may then calculate the ratios of 1,4- to 1,2- and *trans*-1,4- to *cis*-1,4-addition products in these polymers. Figure 8 gives a plot of $\log_e 1,4/1,2$ *vs.* $1/T$. Figure 9 gives a plot of $\log_e$ *trans*-1,4/*cis*-1,4 *vs.* $1/T$.

Having developed methods for the determination of percentage 1,2- and *trans*-1,4-, it is now possible to calculate differences between free energies of activation for 1,4- *vs.* 1,2- and *trans*-1,4- *vs.* *cis*-1,4-polymerization processes. Free radical propagation reactions in butadiene polymerization proceed through the formation of an intermediate allylic free radical. This radical is a resonance hybrid of the two forms:

$$-CH_2-CH=CH-CH_2\cdot + -CH_2-CH-CH=CH_2$$

Both the reaction leading to 1,4-addition and the reaction leading to 1,2-addition involve the same allylic radical and the same butadiene molecule if we neglect possible effects of the *cis*- or *trans*-configuration of the radical or butadiene molecule on the proportions of 1,2- and 1,4-addition. The reactions may be represented as:

$$R-B\cdot + B \xrightarrow{k_{1,4}} R-B_{1,4}B\cdot$$

$$R-B\cdot + B \xrightarrow{k_{1,2}} R-B_{1,2}B\cdot$$

From studies carried out on the variation of the ratio of 1,4- to 1,2-addition with temperature of polymerization, the difference between the free energy of activation for 1,4- and 1,2-forms may be calculated. Results obtained are given by the equations:

$$\Delta F_{1,4}^{\ddagger} - \Delta F_{1,2}^{\ddagger} = -480 - 0.88T$$
$$\Delta H_{1,4}^{\ddagger} - \Delta H_{1,2}^{\ddagger} = -480 \text{ cal.}$$
$$\Delta S_{1,4}^{\ddagger} - \Delta S_{1,2}^{\ddagger} = 0.88 \text{ E.U.}$$

Thus, the heat and entropy of activation favor 1,4-addition over 1,2-addition. However, both heat and entropy effects favoring 1,4-addition over 1,2-addition are very small.

The free radical polymerization of butadiene to yield *cis*- and *trans*-1,4-addition will next be considered. Butadiene exists in the S-*cis*- and S-*trans*-forms. (This means *cis* and *trans* with respect to the single bond of the butadiene.) Mulliken's calculations show a distinctly greater conjugation energy (2.5 kcal.) for the S-*trans*-form than for the S-*cis*-form[13]. Hence, the S-*trans*-form has greater stability, and lowering the temperature of polymerization increases the concentration of S-*trans*-butadiene. Using the experimental ratios of *cis*-*trans*, free energies, heats and entropies of activation may

be calculated for the following reactions:

$$R\cdot + B_{c,t} \xrightarrow{k_1} RB_t\cdot$$
$$R\cdot + B_{c,t} \xrightarrow{k_2} RB_c\cdot$$

where $B_{c,t}$ refers to the equilibrium mixture of S-*trans*- and S-*cis*-butadiene. The results of calculations of differences between the *cis*- and *trans*-forms are given by the equations:

$$\Delta F_t^{\ddagger} - \Delta F_c^{\ddagger} = -4200 + 10.2T$$
$$\Delta H_t^{\ddagger} - \Delta H_c^{\ddagger} = -4200 \text{ cal.}$$
$$\Delta S_t^{\ddagger} - \Delta S_c^{\ddagger} = -10.2 \text{ E.U.}$$

Thus, *trans*-1,4-addition has a 4.2 cal. lower heat of activation than the *cis*-1,4-. This advantage of a lower heat of activation is offset by an unfavorable entropy of activation. However, in the temperature range from −19 to 97°, the *trans*-1,4-form predominates, increasing with decreasing temperatures of polymerization.

Acknowledgment.—The authors wish to thank V. L. Burger, R. R. Hampton, and W. A. Hermonat for their assistance in carrying out the analytical work and purification of polymers.

SUMMARY

Infrared methods have been used in determining 1,2- and *trans*-1,4-addition in polybutadiene polymerized in the temperature range −19° to 97° and butadiene-styrene copolymers prepared at −18°, 5° and 50°. *trans*-1,4-Addition increases and 1,2-addition decreases with decreasing temperature of polymerization. At −19°, substantially all of the 1,4-addition product is present in the *trans*-1,4-form. Approximately 20 per cent 1,2-addition occurs at this temperature and is concluded to account for the major part of the non-crystallizable portion of polymers made at low temperatures. The influence of styrene on 1,2- and *trans*-1,4-addition in butadiene-styrene copolymers is also discussed. Free energy, heat and entropy of activation are calculated for 1,4- *vs.* 1,2-addition and *trans*-1,4- *vs.* *cis*-1,4-addition in the polymerization process.

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SOME PROBLEMS INVOLVED IN THE GRADING AND TESTING OF NATURAL RUBBER. A PROGRESS REPORT *

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INTRODUCTION

The justified demand of the manufacturing user of natural rubber for a material of better quality has become more insistent during the years since the resumption of large-scale plantation production in the areas formerly in Japanese occupation. The present work is part of a program intended to lead directly to a satisfaction of that demand.

The term "quality" used of raw rubber in its solid form may include the following properties.

1) Cleanness
2) Processibility of unvulcanized materials
3) Properties of vulcanizates prepared from the rubber.

Work is proceeding in all three fields; the present paper is mainly concerned with properties of vulcanizates.

PROPERTY TO BE MEASURED

In drawing up a specification for the testing and grading of rubber from this point of view, it is necessary at the outset to decide which property or properties of the vulcanizate are to be used as a criterion of the quality of the rubber itself. It is desirable that the measurements should be of primary physical properties which are known to be important in common uses of rubber, and which can be measured with a high degree of accuracy. On these grounds, tensile strength measurements are not acceptable. A great deal of work has been done practically throughout the present century which has been aimed at measuring the variability of raw rubber by reference to the stress or so called modulus of standard vulcanizates at elongations upwards of 500 per cent. This type of measurement is not considered suitable as a grading test since it evaluates the vulcanizate in a physical condition which actually occurs in very few practical applications of rubber. The phenomenon of crystallization by stretching does, indeed, change the physical nature of the test-piece very considerably, and differences found between rubbers under these conditions alone may well be quite irrelevant to the majority of uses of the material. Measurements of stiffness at elongations below, say, 250 per cent are not subject to these criticisms, and at the outset it was felt that they might well form the basis of an evaluation procedure. Properties of rubber such as abrasion resistance, flex-cracking, or cut growth, which are of paramount importance in

* An original contribution. This paper was presented before the Division of Rubber Chemistry at the 116th Meeting of the American Chemical Society at Atlantic City, N. J., September 18–23, 1949.

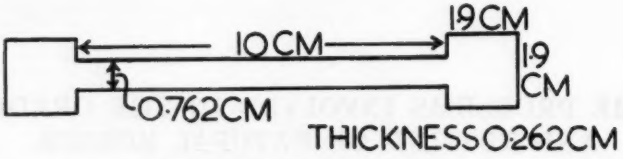

FIG. 1.—Dimensions of strain test-piece.

the service behavior of tires, are not suitable for grading purposes because of the inherent difficulties of such measurements, and also because of the difficulty of correlating laboratory tests with service performance. A grading procedure must be concerned with tests which can be carried out rapidly and accurately, and this is certainly not true of abrasion and flexing measurements.

Having decided that some form of modulus test at a comparatively low elongation would be useful for grading purposes, it is next necessary to specify the test method. Such a method must be rapid and accurate, and should involve relatively simple apparatus. On the grounds of rapidity and accuracy the strain test devised by the U. S. National Bureau of Standards[1] has been shown to have high merit. The essence of this test is the measurement of the elongation of a test-piece at a standard time after the application of a fixed

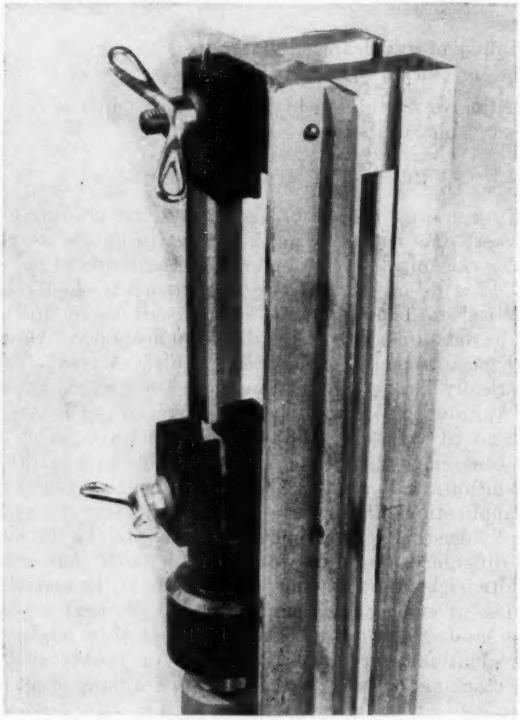

FIG. 2.—Grips of simple strain test machine.

stress. It has been demonstrated that the experimental error in such a test is small, less indeed than that encountered in the conventional modulus test for rubber at high elongations. Since tests for grading purposes will be made on a standard test compound, the principle of the strain test may be used to design an extremely simple and rapid test, the equipment for which may be constructed very cheaply.

SIMPLE STRAIN TEST METHOD

The test-piece, Figure 1, of similar shape but larger in size than the well known T-50 test-piece, is molded. Using a suitably designed mold it is possible to produce test-pieces from a standard compound with a tolerance of ± 1 per cent on all the important dimensions. In practice it is, therefore, unnecessary

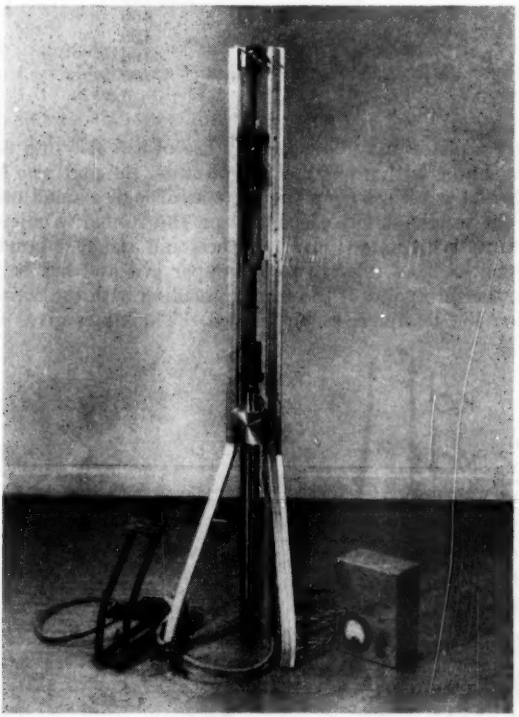

FIG. 3.—Simple strain test machine.

to take thickness measurements and to use these for load adjustment or calculation of final results. A considerable saving in time is thus effected. Each end of the test-piece is located positively in a shaped jaw and a second clamping jaw screwed down to grip along the line dividing the wide and narrow portions of the rubber (see Figure 2). The upper jaw is fixed to the stand, and the lower jaw with its extensions has a standard weight, *e.g.*, 1 kilogram. A plat-

TABLE 1

ERRORS DUE TO END EFFECT

Mold charge	Test-piece	Percentage extension	
		By inch marks	By jaw separation
1	1	104	106.4
1	2	100	103.1
1	3	104	102.6
1	4	104	101.3
1	5	100	101.5
1	6	104	105.7
Mean		*102.7*	*103.4*
Standard deviation		*2.06*	*2.15*
2	1	104	106.4
2	2	100	101.3
2	3	100	98.5
2	4	100	99.5
2	5	100	99.5
2	6	108	109.8
Mean		*102*	*102.5*
Standard deviation		*3.30*	*4.56*

form carried by a piston may be raised by use of a foot-pump to support the lower jaw system and, with a test-piece in position, the platform falls smoothly when air is allowed to escape from the system through a small orifice. At the instant when the weight is left suspended on the rubber, a microswitch built into the platform is actuated, and an electronic timer is started. A scale graduated in mm. is fixed relative to the upper jaw and lies behind the jaws and test-piece, the zero point of the scale coinciding with the top surface of the lower jaw when the test-piece is unstrained. The timer gives a signal after

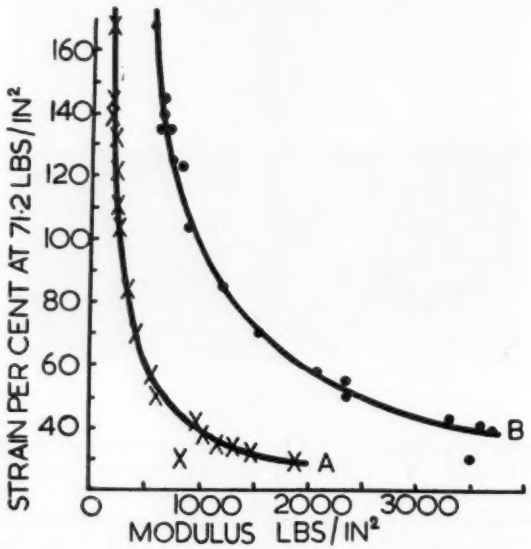

FIG. 4.—Strain *vs.* modulus, A at 500, B at 700 per cent elongation.

1 minute, and the position of the upper surface of the lower jaw is read off from the scale. Since the test-specimen has an effective length of 10 cm., the reading in mm. is the percentage extension of the test-piece. Figure 3 shows the machine in use.

A possible source of error lies in the method of gripping the test-piece. Stress will be inhomogeneous in the region of the grip, and there will also be a tendency for the sample to pull out slightly when under load. To check the behavior in this respect, simultaneous measurements of jaw separation and extension of a section of the rubber defined by normal inch marks have been made. The results (see Table I) show that the error is negligible. The relationship between strain figures and normal modulus results is illustrated in Figure 4. These results were obtained on a range of gum stocks through a wide range of cures.

TEST COMPOUND

The choice of a compound to be used for evaluating raw rubbers is governed by a number of considerations, some of the more important of which are that:

1) It must have a high discriminating power for differing rubbers, but must not exaggerate differences which will be unimportant in practice.

2) It must have curing characteristics such as will indicate clearly its rate of curing according to the method chosen for assessing that property.

3) It must be a compound which is insensitive to external factors, *e.g.*, atmospheric humidity.

4) It should bear a close relationship, *e.g.*, in type of accelerator, with commercial practice.

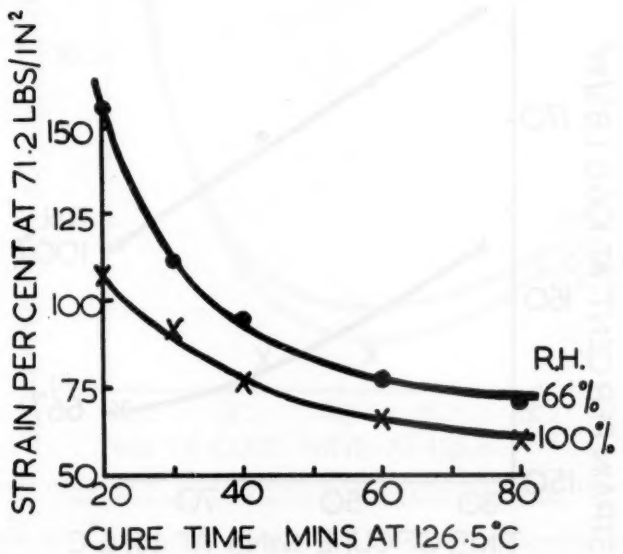

FIG. 5.—Strain *vs.* time of cure, Crude Rubber Committee, American Chemical Society, No. 1 compound (H47) stored at 66 and 100 per cent relative humidity for 7 days before vulcanization

TABLE 2

COMPOUNDING RECIPES

	H47	H46	H49	H41
Rubber	100	100	100	100
Sulfur	3.5	3	—	3
Mercaptobenzothiazole	0.5	0.2	—	—
Diphenylguanidine	—	0.2	—	—
Tetramethylthiuram disulfide	—	—	3	—
N-cyclohexyl-2-benzothiazole sulfenamide	—	—	—	0.75
Zinc oxide	6	6	6	5
Stearic acid	0.5	0.5	0.5	1.0

A considerable amount of published work on the variability of rubber is based on simple rubber-sulfur mixes, while latterly the well known test compound No. 1 of the Crude Rubber Committee of the American Chemical Society[2] has been widely used. A great deal of the earlier work of the British Rubber Producers' Research Association on the subject involves the American Chemical Society Compound No. 1, but experience with this formula raises doubts as to its suitability for grading purposes, mainly because the properties of the vulcanizate are strongly affected by the humidity of storage of the compounded unvulcanized stock. One of many results showing this is illustrated in Figure 5. The behavior of different types of compounds in this respect has been investigated, *e.g.*, H49, a sulfurless tetramethylthiurum disulfide mix; H41, a *N*-cyclohexyl-2-benzothiazole sulfenamide mix; and H46, a mercaptobenzothiazole-diphenylguanidine mix, the compounding recipes of which are shown in Table 2. Curing curves (Figures 6, 7, and 8) show the effect obtained

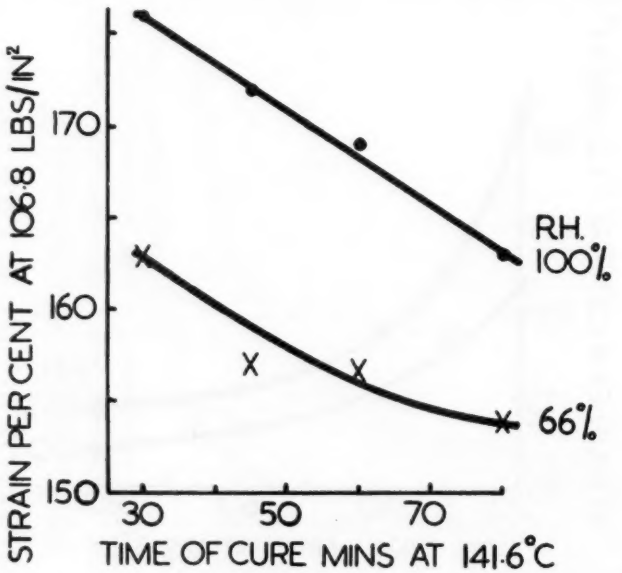

FIG. 6.—Strain *vs.* time of cure, sulfurless tetramethylthiurum disulfide compound (H49) stored at 66 and 100 per cent relative humidity for 7 days before vulcanization.

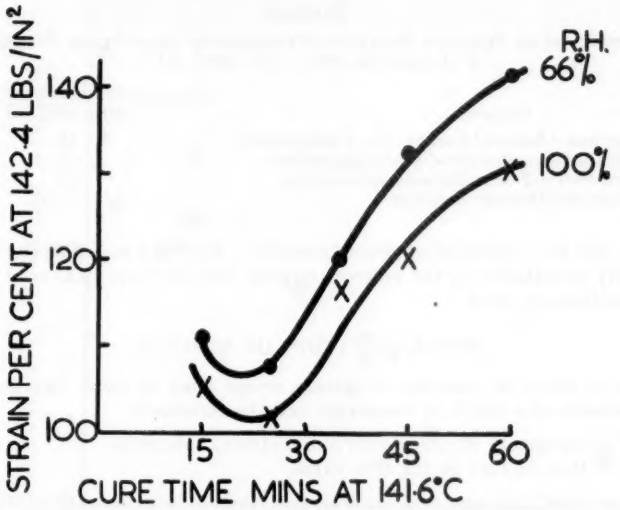

FIG. 7.—Strain *vs.* time of cure, *N*-cyclohexyl-2-benzothiazole sulfenamide compound (H41) stored at 66 and 100 per cent relative humidity for 7 days before vulcanization.

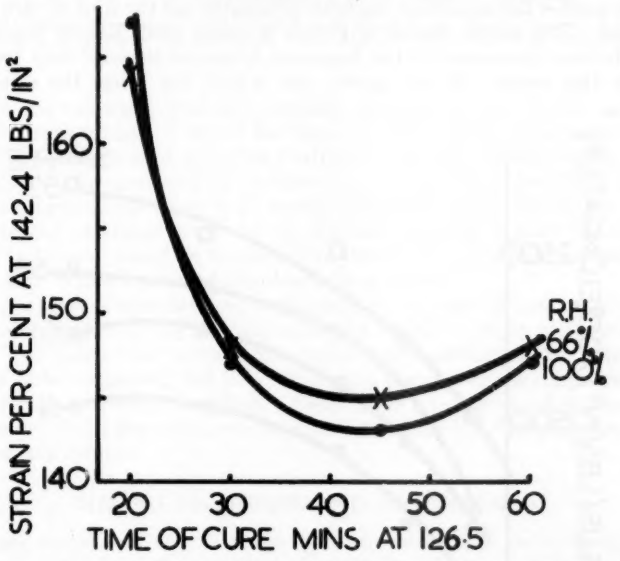

FIG. 8.—Strain *vs.* time of cure, mercaptobenzothiazole-diphenylguanidine compound (H46) stored at 66 and 100 per cent relative humidity for 7 days before vulcanization.

with these three compounds, and Table 3 indicates the proportionate differences in minimum strain between stocks stored for 7 days at 66 and 100 per cent relative humidity, the minimum strain figures being taken from the curing curves for all except the sulfurless H49 compound, in which case no reversion

TABLE 3

DIFFERENCE IN MINIMUM STRAIN OF VULCANIZATE FROM STOCK STORED AT 2 HUMIDITIES (66% AND 100% RH)

Compound	$\frac{\text{Strain 66\% RH} - \text{Strain 100\% RH}}{\text{Strain 100\% RH}} \times 100$
H47 (American Chemical Society No. 1 compound)	18
H46 (mercaptobenzothiazole-diphenylguanidine)	<5
H41 *N*-cyclohexyl-2-benzothiazole sulfenamide	<5
H49 Tetramethylthiuram disulfide	−7.5

is found, the two curves being nearly parallel. The H41 and H46 stocks stand out clearly as suitable for the present purpose, and the latter was used in much of the preliminary work.

INTERPRETATION OF RESULTS

From a curve of modulus or strain *versus* time of cure, two important characteristics of a batch of compound may be obtained:

a) The maximum modulus (minimum strain) attainable
b) The time of cure giving this value.

It is important that any test specification should take account of these two features. The widespread practice of specifying the rate of curing of a rubber by the modulus value at a single cure is not satisfactory, since such a figure indicates neither the maximum modulus attainable nor the time of cure to reach that state. The curves shown in Figure 9, taken from Report No. 2 of the Crude Rubber Committee of the American Chemical Society[2] may be used to illustrate this point. At any given cure within the range the samples are

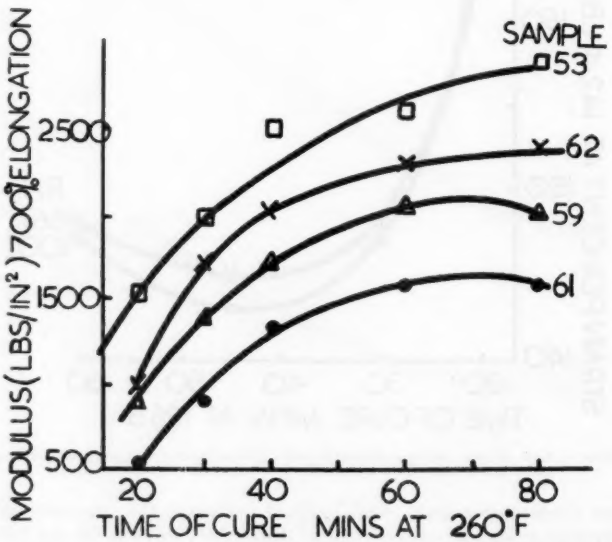

FIG. 9.—Modulus at 700 per cent elongation *vs.* time of cure, American Chemical Society No. 1 compound—4 rubbers.

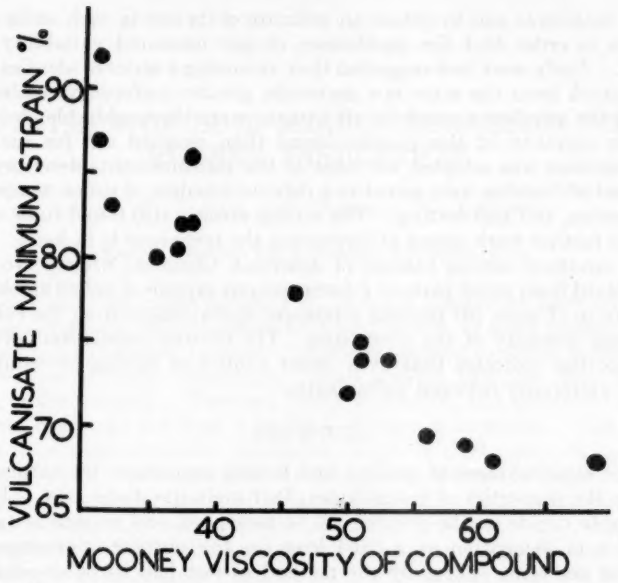

FIG. 10.—Vulcanizate minimum strain (stress 71.2 lb. per sq. in.) *vs.* Mooney viscosity of compound in a series of batches of American Chemical Society No. 1 compound mixed from the same lot of homogeneous raw rubber.

placed in the following order of increasing modulus: 61, 59, 62, 53, and on the above criterion rubber 61 would be classed as slow curing, compared with the rest. The implication of this classification is that two rubbers, say 61 and 53, give equivalent properties if 61 be cured for a longer time than 53. It is clear from the diagram that there is no possibility of rubber 61 attaining a modulus similar to the optimum given by 53, however long the rubber be cured. A sounder judgment would be to classify rubber 61 as a low-modulus fast-curing rubber, and 53 as a high-modulus slow-curing rubber.

For purposes of specification, both modulus and rate of curing are probably best specified indirectly by defining tolerance limits for strain at three specified cures. This matter has not yet been investigated sufficiently for actual specifications to be suggested, but it is interesting to note that a similar method is used in the specification[3] for GR-S. Despite the labor involved, this procedure is considered to be the minimum necessary to define the vulcanization characteristic of the rubber.

MIXING TECHNIQUE AND MIXING ERROR

Mixing error, *i.e.*, the variation between nominally identical batches of compound mixed from the same lots of raw materials, is a well known factor in rubber technology. It is, therefore, somewhat surprising that no account of this is taken in the great majority of published work on the variability of rubber. This neglect means that published estimates of the variability of raw rubber may be inflated by the mixing error to a greater or lesser degree. In the present work an attempt has been made to reduce the mixing error by

suitable technique and to obtain an estimate of its size in each series of measurements in order that the significance of any measured variability may be assessed. Early work had suggested that, in mixing a series of identical batches of gum stock from the same raw materials, greater uniformity resulted if the whole of the powders needed for all batches were thoroughly blended and the necessary quantity of this powder blend then weighed out for each batch. This procedure was adopted for most of the measurements described in this paper, and all batches were mixed to a definite schedule of times, temperatures, manipulation, and mill setting. The mixing error is still found to be considerable, and further work aimed at improving the technique is in hand.

The variations among batches of American Chemical Society No. 1 compound mixed from equal parts of a homogeneous sample of milled smoked sheet are shown in (Figure 10) relating minimum strain (taken from the cure curve) to Mooney viscosity of the compound. The obvious correlation between the two properties indicates that even closer control of mixing procedure would improve uniformity between vulcanizates.

SUMMARY

In the establishment of grading and testing procedures for natural rubber based on the properties of vulcanizates, four main questions arise. First it is necessary to decide on the property to be measured, and reasons are given for the choice of elongation at a fixed load for the purpose, elongations being below 250 per cent. Secondly the method of test had to be decided, and a simple version of the National Bureau of Standards' strain tester has been developed and is in use. Thirdly a standard test mix, into which the raw rubber samples are compounded, must be selected; the well known No. 1 compound of the Crude Rubber Committee of the American Chemical Society has been found to be defective because of its great sensitivity to moisture, whereas a mixed mercaptobenzothiazole-diphenylguanidine stock and a stock accelerated with *N*-cyclohexyl-2-benzothiazole sulfenamide appear suitable. Finally the interpretation of results is discussed. The use of a single cure for classification of rubbers is felt to be inadequate, and to determine both the maximum modulus of which the rubber is capable in the compound and also the cure time to obtain this condition, it is proposed to define the property with tolerance limits at three cures.

Incidental problems arising include mixing error, and some investigation of this is described.

ACKNOWLEDGMENT

This work forms part of a program of technological research undertaken by the Board of the British Rubber Producers' Research Association.

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EFFECT OF SOIL MICROÖRGANISMS ON RUBBER INSULATION *

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Rubber-insulated cables designed for burial in the ground have until recent years been protected from moisture by a lead sheath, as some portions of their length are usually exposed to water. Without the lead covering, failures would result because of water absorption. Lead sheaths have not been a perfect solution of the problem. They are heavy, expensive, and subject to corrosion and electrolysis, and the lead crystallizes if there is vibration. The development of deproteinized rubber insulation, which is electrically stable on long exposure to water, has allowed the direct burial of rubber-insulated conductors in the ground without the need of a lead sheath. Such cables usually are protected mechanically with a rubber sheath of tire-tread type. Many miles of underground and submarine cables insulated with a suitable deproteinized rubber compound have given excellent service for as long as fifteen years. No cable so constructed has failed through water absorption.

Some rare electrical failures have occurred in nonleaded control cables buried directly in the ground. These cables were insulated with a natural-rubber compound having low water absorption. The failed sections showed no direct mechanical injury to the insulation, although in some cases there was a roughening or pitting of the jacket (Figure 1). The failures were characterized by short sections of low insulation resistance. The absorbed water content was no higher than in adjacent sections of normal high insulation resistance, and the physical properties were normal. Drying raised the insulation resistance several decades, but a brief exposure to moisture again decreased it to low values. If the deterioration had been from ordinary causes it would not be expected to be so sharply localized. Although most of the underground environment of buried cables has not caused electrical failure, there have been local deleterious effects on rubber insulation incomparably more severe than any that might be produced even by long soaking in hot water.

SOIL AS ENVIRONMENT

Soil is the habitat of enormous numbers of a variety of microörganisms. According to Frobisher[1], it may contain from 100,000 to 500,000,000 microorganisms per gram. They are mainly in the top layer. Their principal function is the decomposition of organic matter. Until recent years it was not known that microörganisms could utilize the rubber hydrocarbon as a source of food and thereby destroy it.

The earliest cases of attack on rubber by microörganisms cited in the literature were colored spots on raw rubber. These were first attributed to microbes

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living on the various nonrubber impurities, especially the proteins. Söhngen and Fol[2], Novogrudski[3], and Kalinenko[4] discovered that fungi, Actinomyces, and micrococci could utilize purified rubber hydrocarbon as their only source of carbon and energy. Spence and Van Niel[5] showed that the rubber hydrocarbon in latex could be completely decomposed by microörganisms. Zo Bell and Beckwith[6] found that pure cultures of various kinds of aerobic bacteria could utilize several types of raw and vulcanized natural and synthetic rubber. Their criterion of attack was the decrease in oxygen content of an inoculated mineral solution in closed bottles containing rubber.

FIG. 1.—Typical pitting caused by attack of soil microörganisms. Sample after 6-month laboratory soil exposure test (*upper*); cable after 8 years' underground service (*lower*).

There is also a considerable body of literature showing that soil bacteria can utilize many types of hydrocarbons whether straight chain or aromatic, and even materials like phenol[7].

The fact that some soil microörganisms can consume both raw and vulcanized rubber suggested a reason for the cable failures.

ACCELERATED LABORATORY TESTS

Accelerated laboratory tests show that exposure to certain soils destroys the usefulness of rubber compounds as insulation because of soil microorganisms. Conditions especially favorable to this action are active soil, sufficient but not excessive moisture, pH somewhat on the alkaline side, temperatures between 70° and 95° F, and free access to oxygen. Fertile soil contains a great variety of microörganisms in abundance, so that it shows the most drastic action. A slightly alkaline reaction is favorable to most bacteria, and Kalinenko[4] and Novogrudski[3] have shown that the destruction of rubber by microörganisms is most rapid around pH 8. The action of soil maintained at room temperature or slightly above is obviously more drastic than that in cable locations where the ground is warm for only a short period each year. The most useful test was believed to be exposure to all the microörganisms in a given soil rather than to isolated pure strains.

Five test soils were used in the experiments:

1. Railroad cinder fill, pH = 7.5 as received
2. Railroad cinder fill, pH = 7.8 as received
3. Garden soil, pH = 6.0 as received
4. Same soil plus calcium carbonate, pH = 8.0
5. Market garden soil of initial pH 6.5 raised by calcium carbonate to 7.9.

Soils 1 and 2 were from different locations. No. 3 was from a new garden to which no animal manure had been added. No. 5 was especially fertile soil which had been under cultivation for some years. In these tests only whiting and water were added.

Those insulating compounds which were applied by extrusion on wire were tested on No. 14 tinned copper wire with $\frac{3}{64}$-inch wall of insulation. The thin-walled vulcanized latex insulation was applied by the dip process to give a 0.015- to 0.020-inch wall. Six-foot lengths in 2-inch diameter coils with 6-inch leads were first soaked in water at room temperature and their resistance measured. This was to eliminate any defective samples. Parallel exposures were made in most cases in active soil and in tap water. Duplicate coils were placed in each medium in 2-quart wide-mouthed bottles. The soil was packed loosely about the coils and compacted by tapping the bottle. A strip of lead provided contact to the moist soil, which served as a sufficiently conducting electrode. The values of initial resistance of the samples measured in soil agreed closely with those in water.

Although the amount of moisture is not critical, the soil should not be put into the bottles either as a wet mud or as a dry powder. If it is too wet it shrinks away from the sample excessively on drying. This not only produces poor electrical contact, but may also inhibit microbial action because of excessive concentration of curing ingredients, etc., at the surface of the sample. If the soil is put in excessively dry it packs too hard when water is added to make up for that lost by evaporation.

In preliminary tests the samples in water were continued for some months after the samples in soil had failed. This was done to prove that water absorption was not the cause of failure in soil. In the systematic series the tests on samples in water were discontinued as soon as the samples in soil failed, since the primary interest was in the behavior in soil. Previous evidence indicated that failure in soil was not caused by water absorption. Of course, many rubber insulating compounds are not suitable for use in moist locations and would be expected to fail due to water absorption. It is generally easy to separate this effect from failure due to microörganisms.

INSULATION RESISTANCE AS A CRITERION OF ATTACK

The principal difference between the approach in this study and the earlier ones is in the method of measuring microbial attack. Where rubber can be subdivided to provide a large surface, as in the studies of Zo Bell and Beckwith[6] and especially Spence and Van Niel[5], who used latex, the bulk effects produced by microörganisms occur rapidly and measurements of loss of weight of rubber hydrocarbon, increase of acetone extract, consumption of oxygen, etc., afford suitable criteria of attack.

In rubber insulation, where the ratio of area to volume is relatively small, the measurement of decrease in insulation resistance is a test that is incomparably more rapid and sensitive. It is nondestructive, and is less misleading than visual examination. Certain types of insulation, notably GR-S com-

pounds, may develop spots of low resistance as a result of microbial action, with no visible evidence of attack such as pits, roughness, or adhering colonies. On the other hand, particularly with samples immersed in water, growth of microörganisms may be seen adhering to the insulation without harming it electrically.

Tests of insulation failure due to microörganisms by other means than measurement of insulation resistance or dielectric strength might require years to be decisive, or might give negative results, leading to the belief that the insulation was immune to soil exposure. Failed sections of cable have become practically useless electrically without showing appreciable loss of material. Similarly the insulation resistance of many laboratory samples has dropped 10^{-6} and 10^{-8} of the original value, with little or no visible loss of material. This is because microbial attack produces discrete low resistance spots surrounded by intact insulation. These discrete spots may become so dense eventually as to create the appearance of bulk conductivity. The decrease in insulation resistance is so drastic that measurements of high precision are not necessary. Variations of a few per cent with changes in measuring temperature or dampness of the soil, etc., have no significance. Although microbial attack would not be expected to affect samples alike, the checks between duplicate samples are usually rather close.

The resistance of the samples was measured at the prevailing room temperature after 1 minute of stress at 540 volts. For resistance values above 1000 megohms a modified General Radio Type 544-B megohm bridge was used. This measures fairly accurately up to 10^7 megohms. Values below 1000 megohms were measured by a galvanometer.

PROOF OF MICROBIAL ATTACK

Loss of insulation resistance is not in itself proof of microbial attack. Rubber compounds not properly formulated for wet locations may fail due to water absorption alone. Parallel tests were made in soil and water to eliminate this factor. To prove that the deterioration in soil was caused by microorganisms, parallel tests were made on both natural rubber and GR-S compounds in active and in sterilized soil.

The natural rubber insulation in this test was a 0.015- to 0.020-inch wall of vulcanized latex on wire. In one experiment the coils were exposed to tap water, to soil No. 2, and to the same soil steamed 2 hours at 100° C. After exposure for only 1 month in the active soil, the duplicate samples showed a drop in insulation resistance to less than one millionth of the initial value of 10^6 megohms. The coils in both the water and the steamed soil maintained high megohms for 1 year.

In another test two samples of similar wire were placed in No. 4 soil in glass tubes held at a slight incline. Air was bubbled through water, passed through sterile cotton wool, and through the sample tubes to supply moisture and oxygen. One tube was sterilized by heating for 30 minutes in steam at 20 pounds per square inch. The other tube was not sterilized. After exposure for 1 month the sample in active soil showed a decrease in insulation resistance to one millionth of the value shown by the control in sterilized soil. This is evidence that this natural rubber insulation failed because of attack by living microörganisms.

When certain insulating compounds of GR-S were found to fail in No. 5 soil it was desirable to prove conclusively that here too the failure was due to

TABLE I

MEGOHMS AGAINST EXPOSURE OF A GR-S–MINERAL RUBBER INSULATION

	Water	Sterilized soil	Active soil
Initial	3,400,000	3,700,000	3,100,000
	3,500,000	4,100,000	3,200,000
	3,400,000	3,300,000	3,500,000
	.....	3,800,000	3,000,000
	.....	.....	3,300,000
	.....	.....	3,300,000
7 Weeks	4,800,000	3,900,000	0.7
	5,300,000	4,600,000	0.5
	4,200,000	5,300,000	0.6
	.....	5,300,000	0.7
	.....	.....	0.4
	.....	.....	0.6

microbial attack. Thirteen coils of wire insulated with a $\frac{3}{64}$-inch wall of a representative GR-S-mineral rubber compound were put in water, in soil No. 5 not sterilized, and in the same soil sterilized in steam at 100° C for 2 hours. The complete results are given in Table I because of the importance of this test. In the active soil, all six samples failed. None failed in water or in sterilized soil. With these basic results on two types of rubber it seemed unnecessary to run controls in sterilized soil in all experiments. In case of doubt it affords a decisive confirmatory test.

SYSTEMATIC TESTS IN ESPECIALLY ACTIVE SOIL

After considerable exploratory work with different types of compounds in soils of varying activity, systematic tests were made on insulating compounds of natural rubber, GR-S, and Butyl rubber. Soil No. 5 was used as the test medium for the natural rubber and GR-S compounds because it had shown the highest activity toward both in earlier tests. The Butyl compounds were tested in soil No. 4. A series of Butyl compounds corresponding to the natural rubber and GR-S series is under test also in soil No. 5, but it is too early to report the results. All samples were No. 14 tinned copper wire with $\frac{3}{64}$-inch wall of insulation. Four samples of each compound were tested, two in water, and two in active soil.

The natural rubber and GR-S compounds were vulcanized with benzothiazoyl disulfide and zinc dimethyldithiocarbamate, the Butyl rubber series with tetramethylthiuram disulfide and *p*-dinitrosobenzene.

The natural rubber series of eight compounds was made with purified rubber, pale crepe, and smoked sheet with the following additions: mineral rubber, Dixie clay, Atomite whiting, blanc fixe, zinc oxide, talc, factice, and paraffin.

The GR-S series of eleven compounds was made with GR-S-AC, GR-S-65SP, and GR-S-SP with the same fillers and also with reclaim.

The four Butyl compounds were made with GR-I-50BL, mineral rubber, Dixie clay, Atomite whiting, and paraffin.

The insulation resistance of the four samples of each compound was measured initially and after 2, 4, and 16 weeks.

In the three series all samples in water maintained insulation resistance of the initial order of magnitude after 16 weeks' exposure. In the soil, although the rate of decrease varied somewhat, all samples of the three series, natural

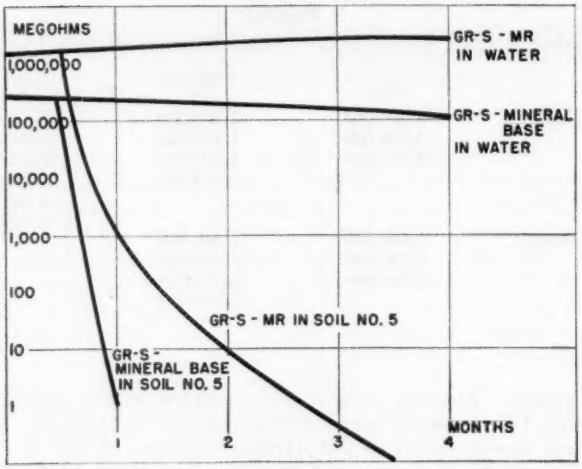

FIG. 2.—GR-S compounds in water and in very active soil.

rubber, GR-S, and Butyl rubber, showed after 16 weeks' exposure a drop in insulation resistance to values between 10^{-6} and 10^{-8} of the initial value.

Although the curves in Figure 2 are plotted for two particular GR-S compounds, they show typical behavior for both GR-S and natural rubber series in soil No. 5. In this soil corresponding GR-S and natural rubber insulations behave alike. This was not true in the case of samples in soils 3 and 4. In these the GR-S compounds maintained high resistance in soil, whereas the natural rubber insulation failed rapidly (Figure 3).

The curves in Figure 4 are typical not only for the Butyl-clay-paraffin compound in soil 4, but almost exactly represent the behavior of the corresponding GR-S compound in soil 5 as well.

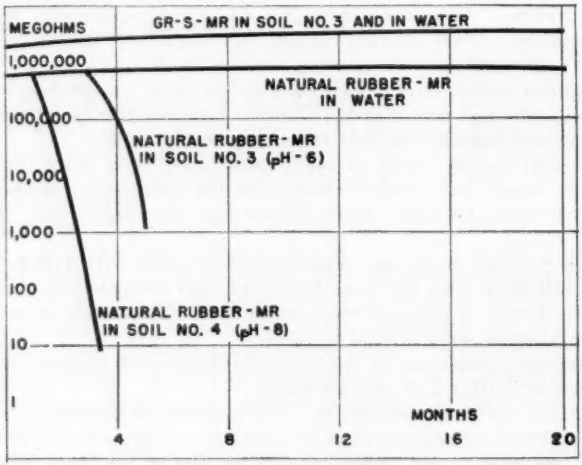

FIG. 3.—Natural rubber and GR-S in moderately active soil and in water.

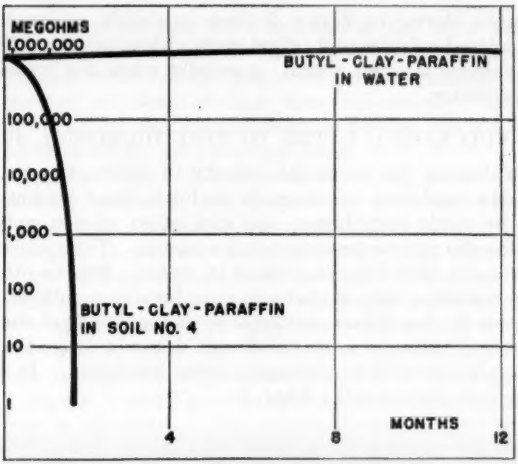

FIG. 4.—Butyl rubber compound in water and in soil.

These results show that the three types of compound were inherently susceptible to active soil regardless of variations in filler type and amount. On the other hand, GR-S compounds appear more resistant than natural rubber compounds to some soils.

LOCATING LOW RESISTANCE SPOTS

The first evidence of incipient failure of a sample of wire exposed to soil is a significant drop in insulation resistance. When this has fallen to 100 megohms or less, many of the minute low resistance spots can be located exactly by means of an electrolytic method.

The coil is placed in a conducting bath containing phenolphthalein. The conductor is made negative, the bath positive. Wherever there is sufficient leakage a pink color appears and gradually expands. Voltages from 100 to 600 volts may be used, depending on the resistance; limiting resistors prevent short circuit. The pink regions in the bath are minute at first. The size and rate of growth indicate the comparative conductivities of the attacked spots. The limit on sensitivity is the diffusion rate of the ions; at extremely low currents the sodium hydroxide is neutralized as fast as it is formed. The bath should be adjusted to a faint pink. If it is acid the test is not sensitive. A mixture of glycerol, water, alcohol, and potassium iodide photographs well. This method of locating low resistance spots shows the exact distribution however numerous the faults. It brings out strikingly the characteristic features of failures produced by the microbial attack.

Figure 5 shows such a test on wire insulated with vulcanized latex made after several months' exposure to soil. Sixty-four leakage spots could be counted. A long time on voltage would show many additional tiny spots, but meanwhile the larger color areas would merge and blur the picture.

This method shows only where the leaky spots are. It is not a direct proof of microbial attack, since pinholes or other low resistance spots could give the same indication. It has to be supplemented by other tests to show that the failures were caused by microörganisms.

In the sample shown in Figure 5 there is visible evidence of microbial attack in the colored colonies and pitted spots characteristic of this insulation. This visible evidence is often absent, especially when the insulation is black and there is no pitting.

USE OF VULCANIZED LATEX TO TEST MICROBIAL ACTIVITY

A means of testing the microbial activity of different environments with respect to rubber insulation is extremely useful in these studies. Vulcanized latex purified by triple centrifuging and applied to wire in walls of 0.015 to 0.020 inch by the dip process provided such a means. This insulation possesses high resistance even after long immersion in water. On the other hand, it is so sensitive to microbial attack that exposure for one month or less to active soil may decrease the insulation resistance to one millionth of the initial value.

Rapid electrical failure of vulcanized latex does not prove that a particular environment is also harmful to synthetic rubber insulation. It should be considered specific only for natural rubber.

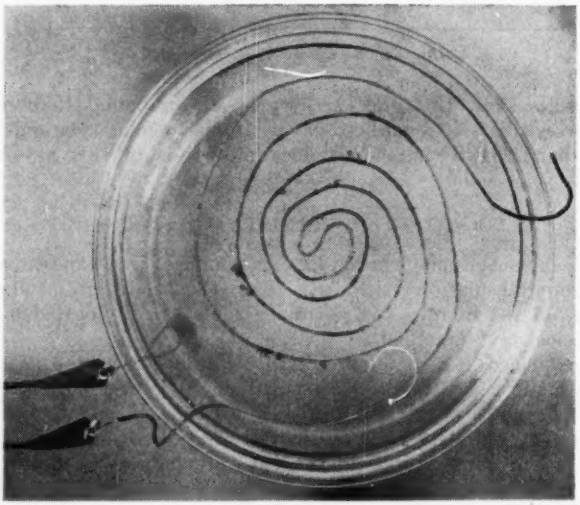

FIG. 5.—Direct current fault-location test on natural rubber insulation attacked by microörganisms.

Various applications of this sensitive test material are described briefly; many more could be devised. The specific activity involved here is the drastic lowering of insulation resistance of natural rubber insulation by microorganisms.

Activity of test soils.—In an ideal laboratory test a given soil would maintain constant activity. It is important in comparing insulations having widely different stability against microbial attack to know whether the particular test soil has lost activity as a result of storage in bottles. Accelerated tests with vulcanized latex showed that long storage in bottles decreases the microbial activity of a soil. In long exposures it is, therefore, advisable to renew the test soil periodically.

A more extensive test was made on samples of earth from two locations in which signal cables insulated with natural rubber compounds had failed.

When attack by microörganisms was suspected as the cause the failed cable sections were no longer available for inspection. Parallel accelerated tests with vulcanized latex insulation in these soils, both as received and sterilized, showed that the soil samples had high microbial activity. The results are plotted in Figure 6. This was strong indirect evidence that the failures of the signal cable had been caused by microörganisms.

Effect of Temperature.—Experiments are being made to determine the lowest temperature pasteurization that prevents microbial attack on rubber insulation. Test coils in active soil were put in an air oven for 24 hours in bottles tightly capped to prevent loss of moisture, then allowed to stand at room temperature. A long exposure will be required to prove that this pasteurization is permanently effective. Any microörganisms having spores able to withstand the heating might develop later and attack the rubber. No failures have occurred so far in any of the test samples after the following heating and room temperature exposures: 1 day 70° C and 3 months at room temperature; 1 day 60° C and 2 months at room temperature; 1 day 55° C and 2 months at room temperature. The retarding effect of mild heating is additional evidence that failures are due to microörganisms.

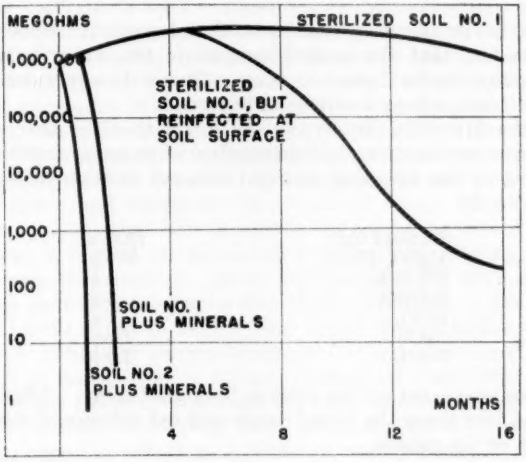

Fig. 6.—Natural rubber insulation in sterilized and in active soil.

Apparently those microörganisms which attack rubber insulation are quite sensitive to heat. Söhngen and Fol[2] and others found that Actinomyces, several species of which are active rubber destroyers, would not survive 5 minutes at 65° C. On the other hand, they are resistant to ordinary drying for at least 6 months. Tests at 37° C showed that this temperature is not high enough to inactivate the microörganisms.

The attack on natural rubber by microörganisms is retarded for a long time by low temperature. Test coils in soil 5 were held at 4.5° C except for a few hours at room temperature prior to resistance measurements. The samples have shown a slight increase in resistance after 4 months.

Effect of Dryness.—As would be expected, soil in a dry state shows less microbial attack on rubber insulation than the same soil when moist. Five test

coils were buried in soil 5 after this had been exposed in a thin layer to room conditions (summer) until it became a dry powder. No water was added. Prior to resistance measurements the samples are removed from the soil and soaked several hours since the dry soil has too high resistance to serve as an electrode. The resistance of all five samples has remained high so far (2 months).

Effect of Reduced Pressure.—As the microörganisms that attack rubber rapidly are aerobic, one would expect that limiting the supply of oxygen would retard attack. In a preliminary study five test coils were embedded in soil 5 in a partial vacuum. The pressure of water vapor plus air fluctuated about an average of 40 mm. Hg. After 17 days the insulation resistance had decreased from 4,000,000 megohms to an average value of 5000 megohms. The coils showed typical attacked spots, but the surface effect appeared less drastic than in a similar coil exposed to the same soil at atmospheric pressure. Zo Bell and Beckwith[6] and Zo Bell and Stadler[8] state that the rate of bacterial oxidation is not influenced until the oxygen is depleted to below 0.3 part per million. It is not surprising, therefore, that microbial attack occurred in the above experiment. This experiment is being repeated under better control by embedding similar coils in moist active soil in glass flasks evacuated to different degrees and sealed off.

Activity of water-submerged environments.—That unsterilized tap water is a relatively safe environment for both natural and synthetic rubber insulation is shown by the fact that the control samples in tap water have maintained normal high megohms for 2 years or more. Obviously any water fit for drinking would not contain large numbers of bacteria.

Inoculated Mineral Solution.—To prove that the absence of failures in tap water was not due to an inhibiting effect of water as a medium, test coils were immersed in the following nutrient mineral solution inoculated with a pinch of soil No. 5:

Distilled H_2O	1000 cc.
$MgSO_4 \cdot 7H_2O$	6.4 g.
KH_2PO_4	1 g.
K_2HPO_4	5 g.
KNO_3	1 g.
$CaCl_2$	Trace
$FeSO_4$	Trace

The leads were protected at the surface by glass tubing. After 5 weeks the resistance was 10^{-5} times the initial value and red colonies of micrococci were clearly visible on the rubber.

So far the authors have not been able to show any microbial attack on GR-S insulation under water. Zo Bell and Beckwith[6] state that Buna-S is attacked as shown by oxygen consumption. It may be that there is a gradual surface attack without colony formation.

Fresh Water Mud.—To measure the activity of a flooded soil as in a fresh water swamp, test coils were buried in active soil which would normally cause the resistance to drop to about 10^{-6} times the normal value in 1 month. The bottles were flooded so that the water level was 2 inches above the soil. The flooding retarded failure for 2 months. After 3 months the resistance had dropped to values of about 10^{-3} times the initial value. Unfortunately, the insulation was not protected at the surface. Examination showed that it was attacked only at that point, but not in the buried portion.

Ocean Bottom Mud.—A similar test was made with flooded ocean mud from Boston harbor. In this case the leads were protected by glass tubing so

that no insulation was exposed at the soil-water and water-air interfaces. The mud was covered with about 1 inch of sea water. Distilled water was added to make up for evaporation. The bottles were left uncovered to permit access of air. This test was intended to simulate conditions at shallow depths near shore, at low tide, etc. The insulation resistance of the test coils has remained high for 14 months.

To simulate ocean bottom conditions at great depths with respect to limited access of oxygen, seven coils were put in ocean mud in a bottle flooded with sea water and closed by a stopper through which a glass tube 5 feet long was passed. This tube was kept filled with water to restrict the diffusion of air to the submerged mud. Of course this arrangement does not subject the mud to the extreme hydrostatic pressure prevailing at great depths. The pressure is believed to be at most a minor factor in microbial attack. That the mud is biologically active is shown by continuing gas evolution and the growth of green algae. After 11 months the insulation resistance of the samples has doubled from an initial average of 5,000,000 megohms. It may be concluded from these results that flooded ocean mud at any depth is a relatively safe environment for natural-rubber insulation as far as bacteria are concerned. The insulation should be protected for some distance above and below the water surface.

In both fresh and salt water the bottom mud generally affords an anaerobic medium. Zo Bell[9] states that little or no oxygen is found in ocean bottom deposits. Henrici[10] makes a similar statement about fresh water mud. This is the result of respiration of the countless microörganisms present in the mud, which produces anaerobic conditions a short distance below the surface. The rubber-destroying microörganisms in general are relatively slow growing ones, which cannot compete with the other types for oxygen in environments where these are numerous and supplied with abundant food. Even in inoculated water this type of insulation may be unattacked for a long time if considerable organic nutrient is present on which the more rapidly growing bacteria can feed, for example, beef bouillon. Rahn and Richardson[11] have shown clearly that in actively growing cultures the solubility and diffusion rates of oxygen in water are too low to maintain an adequate supply except at the surface.

The relative stability of extremely susceptible thin vulcanized latex insulation in dry soil, in flooded soil, or at low temperature shows why cable insulations can last many years, even though the same compound may fail in a few weeks in the accelerated laboratory test. Moreover, the pH would seldom be so favorable to microbial attack as in these laboratory tests.

VISIBLE EFFECTS OF MICROBIAL ATTACK

In addition to the principal tests in which drastic loss of insulation resistance was the decisive criterion of microbial attack, experiments have been carried out to demonstrate the attack visually. Various types of material were exposed to different environments and the growth of colonies, discoloration, pitting, etc., noted.

On natural rubber, particularly on vulcanized latex, the visible effects are striking. GR-S and Butyl compounds, on the other hand, even after drastic electrical failures, generally do not show surface attack.

Bacteriological stains bring out attacked spots on light colored natural rubber, like vulcanized latex, after as little exposure as 4 days in soil. In this study three stains were used directly on the rubber: erythrosin, Loeffler's

methylene blue, and Gram's stains. The stains bring out the colonies vividly. The procedure for determining whether the microörganisms are Gram positive or Gram negative also can be carried out directly on the rubber. It is advantageous to immerse the sample in alcohol before staining, since some microorganisms—for example, Actinomyces—are somewhat water repellent, due to waxy or fatty materials[12], so they do not stain readily. In the Gram procedure this is especially important, because otherwise the colonies might not take the first stain and an incorrect result would be obtained.

Staining is very useful on tests on the resistance to soil microörganisms of paraffin and other compounding waxes. Slides dipped in molten wax to

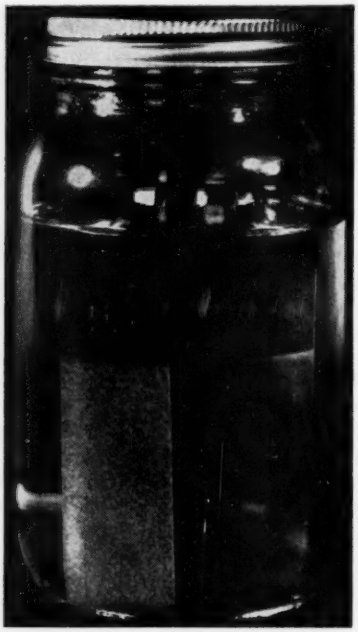

FIG. 7.—Colonies of Actinomyces on natural rubber film.
After 5 days in inoculated water (*left*); and zero days (*right*).

obtain a thin film are exposed to soil or inoculated water. Paraffin is especially susceptible to microbial attack and tends to make insulating compounds more vulnerable.

Although staining produces a striking visual effect when colonies of microorganisms grow directly on the rubber, it is not a general criterion of attack by microörganisms. Some types of insulation, for example, some GR-S compounds, after the insulation resistance has fallen below one millionth of the initial value as a result of exposure to microbially active soil, may neither show colonies nor take stain.

Another case in point is that of failure due to microbial attack in cables having a natural-rubber jacket. The outer surface of the jacket is apparently not perforated, and presumably no microörganisms have contacted the insu-

lation proper. The staining procedure gives negative results on the inner side of the jacket and on the insulation. Nevertheless, the latter has failed and the spots, where it is weak, can be precisely located by the electrolytic method.

One interesting way of exposing various types of raw rubber, etc., is in the form of thin films obtained by dipping microscope slides in a solution. Figure 7 shows a film of purified natural rubber after only 5 days' immersion in mineral solution inoculated with a pinch of No. 5 soil; on the right is an unexposed blank. The numerous spots are colonies of Actinomyces. Figure 8 shows a typical single Actinomyces colony; this was the prevalent type observed in this test. Red colonies of Gram-positive micrococci also form on these films, but are somewhat inhibited by antibiotic action of the Actinomyces.

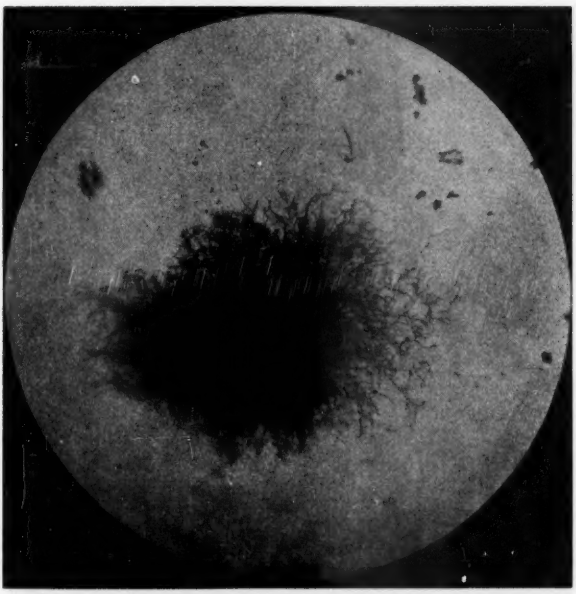

FIG. 8.—Close-up of Actinomyces colony in Figure 7 (100×).

In the course of a few weeks the film became coated with a slime formed by sheathed bacteria, notably Sphaerotilis[1] which apparently feeds on microorganisms that can directly utilize the rubber. A more striking example of indirect utilization is the presence in bacterial colonies of large numbers of protozoa, which under the microscope can be seen busily devouring the micrococci that directly consume rubber.

Films of raw Butyl and GR-S rubber, Neoprene, polyvinyl chloride, and gutta-percha completely immersed in the same medium have remained free of visible microbial growths for several months. When films were partially immersed, a dense intensely white growth of Actinomyces appeared at the water line on the natural rubber. GR-S films showed appreciable fungus growth above the water line; Butyl films showed no apparent growths of any sort. There was a certain mottling of the Butyl film in the submerged area,

but the cause of this is not yet understood. These mottled areas did not take bacteriological stain.

Similar films were placed flat in Petri dishes with the surfaces partially covered with inoculated mineral solution. The most common growth on natural rubber was that of Actinomyces colonies, which were abundant after 1 week. On thin films the colonies moved across the slide leaving clear glass behind them. Attacked natural rubber films stained readily in aqueous erythrosin. GR-S and Butyl films even after some weeks' exposure took no stain.

Vulcanized latex is an excellent material for visual tests. Colonies of considerable diversity of color and form develop on sheets in inoculated water or in soil. The effect shown in Figure 9 was obtained by burying a sheet of

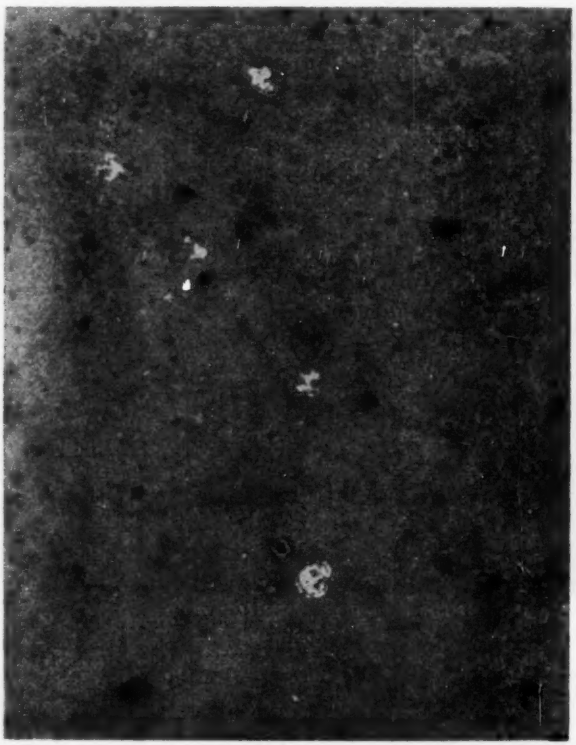

FIG. 9.—Colonies of various soil microörganisms growing on pure-gum natural rubber compound.

acetone-extracted vulcanized latex in active soil for one month. Such colony formation is most abundant when the curing agents and antioxidants are substantially extracted, as these tend to inhibit microbial growth.

They do not, however, protect buried wire samples where a relatively small amount of rubber is exposed to a large amount of soil. This was shown by the invariable failure of the samples insulated with vulcanized latex after one month in active soil. These samples had not been acetone-extracted. When

a number of sheets of the same material were immersed in a bottle of inoculated water no visible attack occurred in over 6 months. The strong smell of leached-out curing agents led to the suspicion that microbial attack was inhibited. After the sheets had been soaked in several changes of hot water and immersed in fresh inoculated mineral solution numerous colonies of reddish Gram-positive micrococci gradually developed. Pieces of these sheets were used as starters to inoculate tanks of solution in which acetone extracted sheets of the same material were floated. Profuse growth of colonies, mostly of micrococci, occurred within a few weeks.

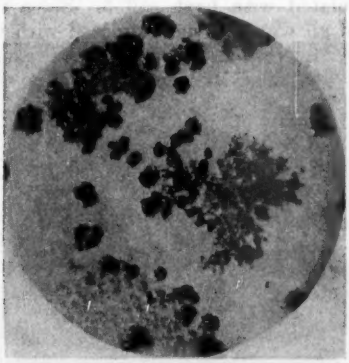

FIG. 10.—Surface of natural rubber pitted by soil microörganisms, early stage (30×).

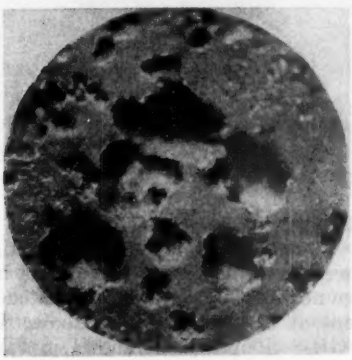

FIG. 11.—Surface of natural rubber pitted by soil microörganisms, advanced stage (30×).

Figures 10, 11, and 12 show the mechanical effects of the attack. This extreme pitting and eating away is characteristic of microbial attack on vulcanized latex. The microstructure of coalescing globules of rubber appears to make this material especially vulnerable. Sheets of press-vulcanized purified natural rubber of essentially similar composition were attacked under the same conditions but much less drastically, even though they too were acetone-

extracted. Press-cured sheets of GR-S gum containing only the necessary curing agents which were mostly removed by acetone extraction showed no attack whatever in the tank of inoculated mineral solution which produced the effects on natural rubber shown in Figures 10 and 11; they took no stain.

This might lead one to the false conclusion that GR-S compounds were completely resistant to microbial attack. Since in this tank the only inoculation was by means of a small piece of infected vulcanized latex, it can be concluded only that those microörganisms that ate large craters in the vulcanized latex did not show any visible effect on the GR-S compound. In other experiments, however, strips of the same GR-S compound were exposed to the mineral solution inoculated with fresh soil 5. Since this is the soil which caused rapid failure of all wire samples insulated with GR-S insulating compounds, the microörganisms responsible should have been present in the inoculated liquid. Nevertheless, the GR-S sheets showed no visible attack or colony

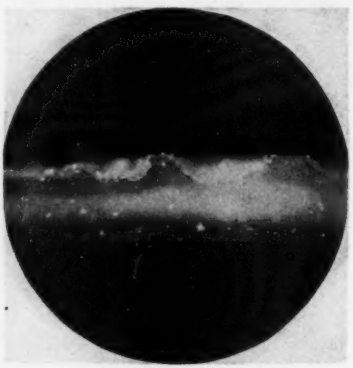

FIG. 12.—Cross-section of pits on sheet of rubber in Figure 11 (30×).

formation after more than 1 month. In another experiment an Actinomyces colony was placed in the middle of a square of acetone-extracted GR-S sheet barely covered with mineral solution. Instead of growing it gradually disappeared.

Above water, insulating compounds of GR-S support the growth of fungus. Such growth was first noted with raw GR-S on partially immersed slides. Fungus appeared above the water line. When coils insulated with GR-S-mineral rubber compounds were placed in inoculated mineral solution no growth appeared except at 0.5 inch or more above the water level. The growth of fungus on GR-S compounds is shown in Figure 13. This was a GR-S-mineral rubber compound having low water absorption. It was moistened, dusted with soil 5 to inoculate it, and placed on sand wet with mineral solution in a closed bottle. The picture was taken after 7 weeks' exposure.

In another set of experiments coils of the same wire were buried in moist soil 5 in closed bottles so that the turns were separated from the wall by only a few millimeters of soil. After less than 2 weeks the turns could be seen outlined in white fungus mycelium. This gives a direct view of what happens at the surface of the wire. It leads one to suspect, although it does not prove, that fungus could have caused the electrical failures of the GR-S samples in

soil 5. A more direct proof is to place coils in soil first sterilized then inoculated with a culture of this, as yet unidentified, fungus. Drastic decrease in insulation resistance in the inoculated sample, but not in sterile controls, would indicate that this fungus is one attacking agent. If this is so it might explain the apparent immunity of GR-S under water.

Lumps of raw GR-S on moist soil 5 in a closed bottle supported abundant fungus growth. When similar pieces of the same raw GR-S were acetone-extracted 24 hours, dried, and placed on the same soil, the growth of fungus was much less profuse but some appeared after 2 weeks. It is not yet known whether the fungus could utilize pure GR-S hydrocarbon.

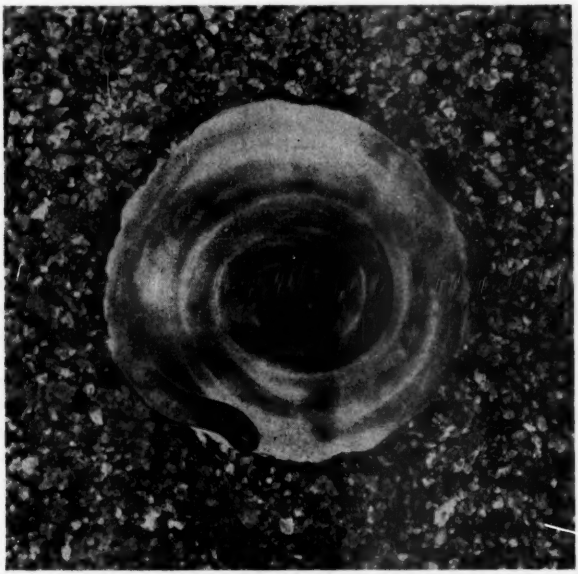

FIG. 13.—Fungus on GR-S insulation.

Raw Butyl rubber does not appear so far to support fungus growth; raw smoked sheet and pale crepe support abundant fungus growth. Purified natural rubber in shreds mixed with soil 5 shows slow fungus growth, much less than GR-S. Practically no growth has been observed on the vulcanized latex in any environment. This material seems most susceptible to aquatic bacteria and to Actinomyces. Figure 14 shows a purified natural rubber-mineral rubber compound after a few weeks in inoculated mineral solution in a Petri dish. Here the prevailing microörganism is Actinomyces.

A great deal of work was done during World War II on the effect of fungus on various rubber and plastic materials. Leutritz[14] shows that, in spite of abundant fungus growth on insulating plastics exposed to high humidity, the resistance is restored by drying. From visual and microscopic examination he concluded that the materials had suffered no damage.

Stief and Boyle[15], in a study of fungicides in rubber, show negligible effect

of soil burial on the physical properties (tensile, elongation, etc.) of natural rubber, GR-S, and Neoprene.

Two points in this connection should be clarified. The main emphasis in the published reports on the effects of fungus has been on the physical damage or the electrical surface leakage. This study is concerned exclusively with leakage through cable insulation in locations where it cannot be kept dry. Drying laboratory samples which had failed in moist active soil temporarily restored the normal insulation resistance, but this has no practical significance for moist environments because the resistance would fall to the low value after a few hours of exposure.

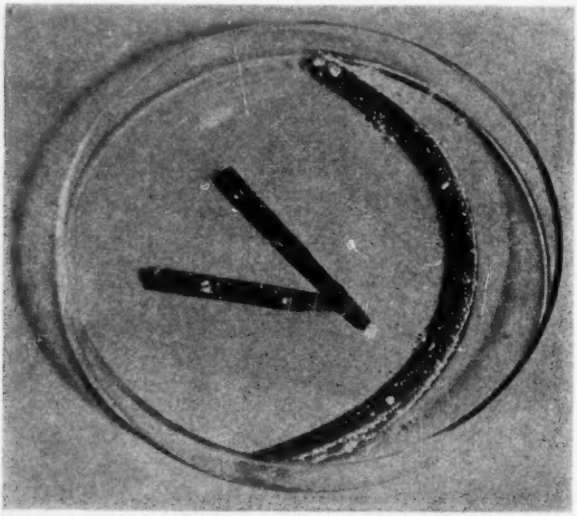

FIG. 14.—Growth of Actinomyces on natural-rubber insulation.

The other point is that as a result of soil burial the insulation resistance may fall to excessively low values with no visible mechanical effect, and with no significant decrease of tensile, elongation, etc. This is why the insulation resistance measurement affords a more searching and a more significant criterion of the stability of insulation continuously exposed to soil.

Zo Bell and Beckwith[6] point out that substances which are bacteriostatic by themselves may not be effective when compounded with rubber. The results of Dimond and Horsfall[16] have been cited by several authors to suggest that tetramethylthiuram disulfide (Tuads) might protect rubber compounds against microbial attack. Dimond and Horsfall did not test this material in rubber, but merely sprayed a water suspension on glass slides, which were then inoculated with spores of a single fungus species. It was found to inhibit growth, both alone and together with zinc oxide. From this result it was concluded that it would be advantageous in rubber compounds as protection against microbial attack. The failures of all the Butyl compounds which contained tetramethylthiuram disulfide show that it does not protect rubber insulation exposed to active soil. It might do so if such insulation were exposed merely to high humidity.

There is also especially convincing visual evidence. A piece of a failed sample insulated with Butyl rubber was rinsed and placed in a Petri dish in mineral solution. In a short time it became covered with a variety of microorganisms, notably fungus and Actinomyces, and the pellicle characteristic of attack on paraffin appeared on the water surface.

Mechanism.—The exact mechanism by which microörganisms cause minute channels of low electrical resistance through a wall of rubber insulation is obscure. The damage appears to extend beyond the regions actually contacted by the microörganisms. For example, in a failed cable the jacket may be only slightly pitted on the outer surface with no detectable perforations; the insulation underneath may appear intact yet show the characteristic low resistance spots.

Preliminary tests in which susceptible insulation has a thin barrier between itself and the active soil seem to indicate that the microörganisms do not need to consume the insulation nor even contact it directly. Since the types that cause deterioration of rubber insulation were present in the soil before the rubber was put in, it is obvious that they do not require rubber for nourishment. The necessary organic foods are already abundant in fertile soil.

Microörganisms are known to break down various materials into forms capable of diffusing through their cell walls. This they do by means of enzymes[17]. Enzymes are proteins and generally are colloidal, so although they may attack the rubber surface and cause progressive decay, they would not be expected to diffuse through it readily. This makes it seem unlikely that the low-resistance channels are caused by the actual presence of enzymes. However, there may be degradation products that can diffuse. The manner in which the effect can take place through a resistant barrier is also puzzling; more rigorous experiments with barriers are necessary to establish the reality of this effect.

The absence of minute holes has not yet been definitely proved. The possibility of the presence of defects that make certain spots more susceptible to microbial attack is also under study.

TESTS ON MATERIALS OTHER THAN RUBBER

Gutta-percha has shown somewhat greater stability than natural rubber, either raw or compounded. Thin films on glass slides showed no growths of colonies either in soil or inoculated mineral solution. On wire exposed to active soil 5, the insulation resistance of four samples has dropped after 5 months to about 0.01 of the initial value, whereas in the two control samples in water the resistance has remained constant. It is known that gutta-percha deteriorates unless stored under water. The deterioration of the samples in soil may be due to ordinary oxidation rather than to microbial attack. Parallel tests in sterilized soil which would be necessary for a conclusive proof of microbial attack were not made. The large resin content would be expected to have some effect on the rate of microbial attack.

The insulation resistance of wire samples insulated with polyethylene and with polyvinyl chloride has remained high and practically constant after 2 years' exposure to soils 3 and 4 (pH 6 and 8). A recent report[18] states that polyvinyl chloride insulation showed good physical and electrical properties after 12 years' exposure to soils of pH 4.8 and 5.3. Because of the acidity of these soils, microbial attack might be suppressed. In soils 3 and 4, however, such attack would be favored. Thus polyvinyl chloride insulation appears to be stable in various soils.

In view of the much higher activity of soil 5, a large number of polyethylene- and polyvinyl chloride-insulated samples are under prolonged tests in it.

Neoprene compounds appear to be inherently resistant to soil exposure. The proper function of Neoprene compounds is as a protective covering rather than as insulation. The initial values of insulation resistance are so low that any effect of attack by microörganisms is masked. The most significant tests of Neoprene compounds are made by applying them in a thin layer over insulation known to be susceptible to microbial attack, burying the samples in soil, and measuring the insulation resistance of the combination periodically.

SUMMARY

Evidence is presented that some of the rare failures of nonleaded rubber-insulated underground cables were caused by soil microörganisms. Laboratory conditions deliberately chosen to favor microbial attack made possible greatly accelerated tests in which failures like those found after ten years or more in service have been produced in a few weeks or months. These failures are characterized by discrete, minute low resistance spots. Drastic decrease of insulation resistance was used as the criterion of failure. The exact distribution of low-resistance spots has been shown by an electrolytic test. Parallel tests in sterile and in active soil proved that the failures in soil were caused by living microörganisms. Soil exposure tests have been made on natural and synthetic rubbers and several other plastic insulations. Natural rubber compounds were found to be the most susceptible. In some soils GR-S compounds proved stable up to two years, but failed in a more active soil. The exact mechanism of attack is not known. In some cases there is drastic electrical failure without visible surface effect. In actual operation of underground cables the exact combination of conditions necessary for producing failure by microbial attack can occur only rarely. The purpose of the severe laboratory tests is to make possible the development of insulations stable under all soil conditions.

ACKNOWLEDGMENT

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TEAR INITIATION AND TEAR PROPAGATION *

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In a previous paper[1] it was shown that the mechanism of tearing is not the same with all rubbers and some rubbers have a tendency to develop knotty tears. In fact, the good tear resistance of Butyl rubber at elevated temperatures can be explained on the basis of development of knotty tears. Having obtained a knotty tear with a natural rubber "gum" stock and having proved that structure effects between carbon black and rubber micelles are not necessary prerequisites of knotty tears, it is probable that rubbers containing different fillers have different mechanisms of tearing. It is well known that some fillers produce a marked grain effect, but, in addition, the present investigation has shown that certain nonblack fillers have a tendency to give knotty tears.

To improve the accuracy of the crescent tear test, a new and improved I.C.I. tear cutter has been developed[2], and this cutter was used in the present work.

The opportunity has been taken to compare the angle tear method[3] with the more widely adopted crescent tear method[4]. The suggestion has been made[2] that the angle tear method gives a measure of tear initiation, whereas the crescent method gives a measure of tear propagation. Some authors[5] are of the opinion that tear initiation is more important than tear propagation, and they favor the angle method for this reason. Studies of tear initiation are undoubtedly important, and one day it may be possible to suggest methods of delaying and preventing tear initiation; at the present time, however, tears and cuts are initiated by many different mechanisms, e.g., ozone cracking, flexing, and penetration of sharp objects into the rubber, and the problem of tear propagation would exist even if improvements in tear initiation were made. In the present author's opinion, therefore, the relative importance of the two types of test is largely a debating point, and in practice both types are important and should be studied. The angle method can, therefore, never be considered as a replacement for the crescent method, and later in this paper some of the defects of the angle method are discussed. The I.G. tear test[6] using nicked Schopper rings has also been included in the present investigation to classify this method, which was in general use in Germany.

CLASSIFICATION OF TEAR TESTS

Tear tests have been classified into the following two main groups[7]: (1) direct tearing; and (2) tearing perpendicular to the direction of stretching.

The first group is analogous to ply-separation tests, where the width of the sample torn is unimportant, but in the second group the force required to tear the test-piece increases as the width is increased; therefore the width of the sample is an important dimension in the case of group (2) test-pieces. It was, therefore, suggested that the results of group (2) tests should be expressed as

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kgs. per sq. cm. or lb. per sq. in. so as to take the width of the sample into account. During discussion of this test for inclusion in the revised draft of B.S. 903, it was agreed that it would be better to express the result as a load corrected for standard thickness and width. The standard thickness and width chosen were two millimeters and one centimeter, respectively.

The crescent, angle, and I.G. tests are all group (2) tests. My contention that the width of the test-pieces was important in the crescent sample has been doubted by Taylor[8], who has raised the point that the data given in Figure 24 were obtained using straight strips[1]. The work on the effect of depth of nick

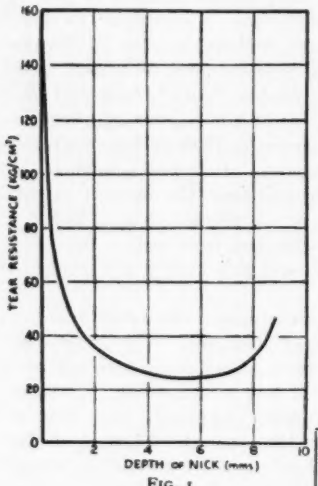

FIG. 1

FIG. 3

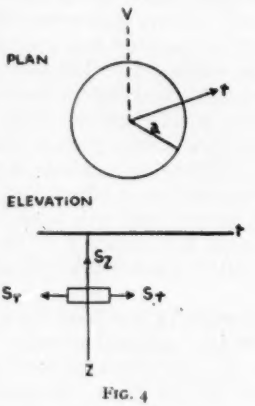

FIG. 4

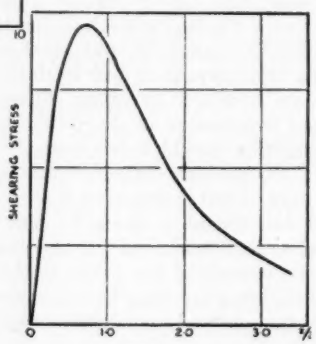

FIG. 5

FIG. 1.—Depth of nick *vs.* tear resistance for crescent-type tear samples. FIG. 3.—Schematic diagram of the progress of tear in test sample with fibering present. FIG. 4.—Schematic diagram for mathematical analysis of load distribution over circular area on a plane surface. FIG. 5.—Shearing stress aganist depth *z/a*.

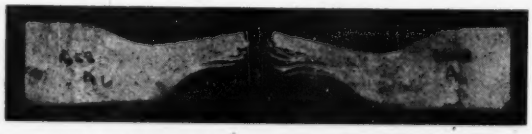

FIG. 2.—Fibering in Butyl rubber sample containing 80 volumes Winnofil

has now been repeated, using crescent test-pieces. The results are given in Figure 1 and show conclusively that the crescent test is indeed a group (2) test; therefore the width must be taken into account when expressing the results.

A point not sufficiently realized is that, although a tear test may be classified as a group (1) or a group (2) test, the classification may alter during testing if knotty tears occur. When a knotty tear develops, either a direct tear becomes a perpendicular tear or a perpendicular tear becomes a direct tear. In other words, when a knotty tear develops in a group (1) test, the test becomes a group (2) test. Similarly, a group (2) test can be converted to a group (1) test. In most cases, therefore, where straight tearing does not occur, the test is a mixture of group (1) and group (2) tests. This is one reason why the earlier suggestion[1] that the tear resistance should be expressed as:

$$T = \frac{L}{t \times D}$$

(where T = tear resistance
L = applied load
t = thickness
D = distance tear travels),

did not explain all the anomalous results obtained with knotty tears. In fact, it is now clear that this contention applies only to cases where knotty tears occur in a group (1) test or with a straight tear in a group (2) test, and the method should not be used with knotty tears in group (2) tests. Even in a group (1) test it is only the knotty part of the path which should be taken into account.

DIFFERENT TYPES OF KNOTTY TEARS

Previously[1] the different types of knotty tear obtained with a crescent test-piece were discussed fully. One further example deserves mention at this stage, and this is the case of fibering which occurred with a sample of Butyl containing 80 volumes of Winnofil (see Figure 2). It was noted previously that Butyl rubber had a marked tendency to develop short direct tears in the direction of stretching. In this series of experiments the number of direct tears increased as the volume loading of the Winnofil was increased until, at high loadings, the rubber fibered at the high elongations. It has been pointed out[9] that when Butyl is under a high strain, the material becomes anisotropic; and when a pin is inserted into the rubber, it can be moved along the fibers (*i.e.*, in the direction of stretch) relatively easily, whereas it cannot be moved across a fiber. This condition merely shows orientation in the direction of stretching and must not be taken as an indication of crystallization, since the same tendencies can be found with GR-S samples. A greater degree of orientation increases the cohesive forces between fibers, as the fibers are packed closer together. It seems probable that the cohesive forces between fibers or chains reach a limiting value, and then the structure is locked in such a way that any additional force deforms the structure in an analogous way to the deformation of a crystal lattice. In other words the forces applied first of all produce maximum packing; then additional force is required to rupture a chain or groups of chains. This explanation is in accord with the types of knotty tear obtained with Butyl rubber and fully explains the observed phenomena.

Considering further the development of this fibering as the tear proceeds across the test-piece, let us assume that, in Figure 3, the tear starts from the

base of the cut in the region of A, and continues, roughly speaking, in a straight line until point B is reached. At point B the lateral tension t_2 reaches a value where it exceeds the secondary forces holding the fibers or chains together, and a direct tear starts at B. As this tear proceeds, the tension t_2 relaxes and is dissipated until the tear at B cannot proceed further. Meanwhile, during this time the other component of the tension t_1 is increasing and produces further packing, which helps to increase the resistance to the direct tear at B. When the tension t_1 reaches a value in excess of the rupture strength of individual fibers or groups of fibers, a straight tear starts at point C and proceeds to point D. At point D the tension t_2 is again sufficient to split the fibers, and another direct tear starts. This process continues until the sample is torn across the complete width. The number of direct tears and their spacing is controlled by the rate of propagation of the direct tear and the corresponding relaxation of the tension t_2, along with the rate of build up of tension t_1 in relation to the strength of individual fibers or groups of fibers.

One may ask why this phenomenon is not observed with other rubbers. The correct answer is that a few examples of natural rubber have been found to fiber, but they occur infrequently. This point would indicate that the secondary forces in the case of other rubbers are higher than those of Butyl rubber and approach more nearly the order of the rupture strengths of the actual fibers. This is confirmed by the data quoted in the following table[10].

TABLE 1

	Covalent bond energy along the chains (Cal./mol.)		Molar cohesion per 5Å. chain length with coördination number four (Cal./mol.)	
Natural rubber	—C=C—	70–120,000	$(CH_2)(CH{=}C\cdot CH_3)$	1,300
Neoprene-GN	—C=C—	70–120,000	$(CH_2)(CH{=}CCl)$	1,600
Butyl	—C—C—	70–80,000	$(CH_2)(CH_3)$	1,200

SUBSURFACE STRAIN

Evidence has been put forward[1] that the degree of strain is not uniform throughout the thickness of the sample. Many new examples illustrating this phenomenon have been found in the present work. Recognizing that, in the case of a load distributed over a small area of a plane surface, the maximum shearing stress does not occur at the surface but at some distance below the surface, the practical evidence can be summarized as follows. After rupture, some samples show a straight line down the center of the ruptured surface; others show a definite fracture in a subsurface plane, and others, typical examples of which are given in Figures 9, 10, 13–17, show a tongue-shaped tear where the peaks and valleys locate the line of maximum shearing stress very exactly.

Problems similar to these have been tackled mathematically, and the following solution has been worked out for a simple case[11].

Consider a load distributed over a circular area of radius a on a plane surface (see Figure 4).

If q is the load applied over the area the stress components are given by

$$S_z = q\left[\frac{z^3}{(a^2+z^2)^{\frac{3}{2}}} - 1\right]$$

$$S_r = S_v = \frac{q}{2}\left[\frac{2(1+Q)z}{(a^2+z^2)^{\frac{1}{2}}} - (1+2Q) - \frac{z^3}{(a^2+z^2)^{\frac{3}{2}}}\right]$$

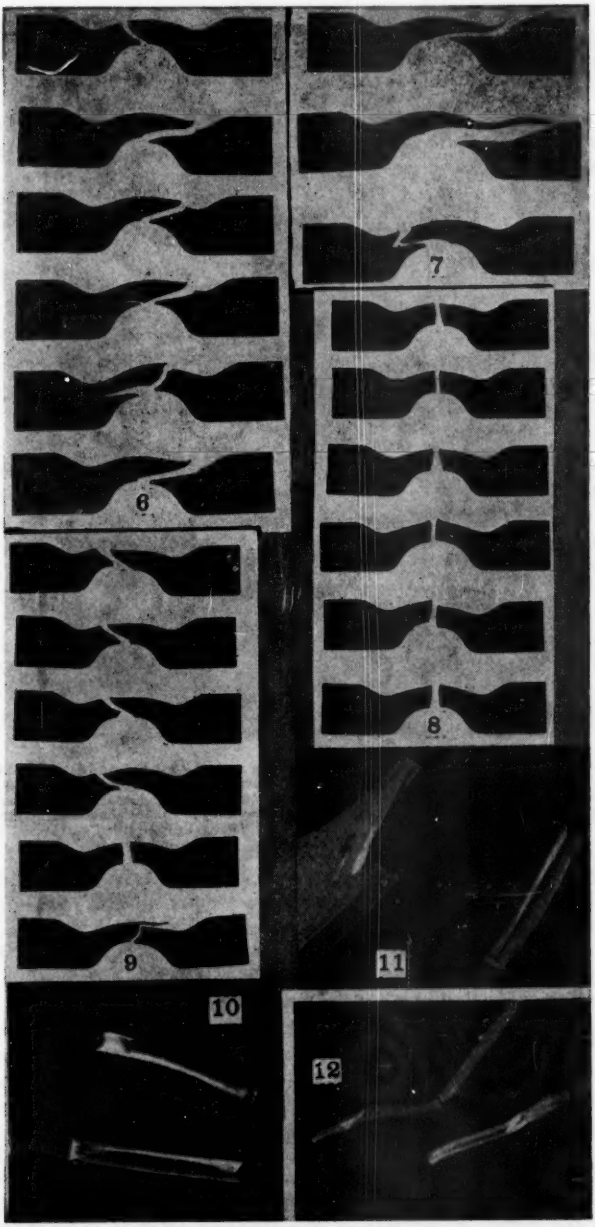

FIG. 6.—Direct tear and knotty tear in GR-S containing 150 parts Calcene. FIG. 7.—Development of direct tear into knotty tear. FIG. 8.—Example of poor tear resistance of Butyl rubber containing china clay. FIG. 9.—Poor tear resistance of Butyl rubber containing 300 parts whiting. FIGS. 10, 11.—Maximum shear stress development in subsurface plane of natural rubber with Winnofil. FIG. 12.—Pronounced tongue tear in angle test piece—natural rubber.

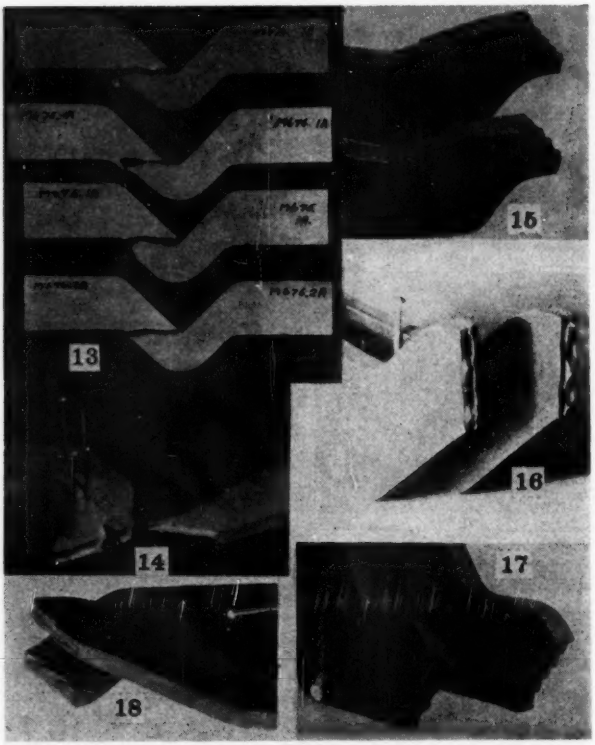

FIG. 13.—Tear along lines of applied force in angle tear sample—natural rubber. FIG. 14.—Evidence of maximum shear stress in two planes at right angles—natural rubber. FIG. 15.—Serrated-edge type of tear—Kosmos-20 carbon black in natural rubber. FIG. 16.—Angle tear specimen showing three stress planes—natural rubber. FIGS. 17, 18.—Serrated-edge tear—natural rubber containing Magecol.

where Q is Poisson's ratio.

The shearing force is given by:

$$\tau = \tfrac{1}{2}(S_v - S_s) = \frac{q}{2}\left[\frac{1-2Q}{2} + (1+Q)\frac{z}{(a^2+z^2)^{\frac{1}{2}}} - \frac{3}{2}\frac{z^3}{(a^2+z^2)^{\frac{1}{2}}}\right]$$

This becomes a maximum at $\left(\frac{\delta\tau}{\delta z}\right) = 0$.

Therefore we have:

$$\frac{z}{(a^2+z^2)^{\frac{1}{2}}} = \tfrac{1}{3}[2(1+Q)]^{\frac{1}{2}} \quad z = a\sqrt{\frac{2(1+Q)}{7-2Q}}$$

Hence

$$\tau_{max} = \frac{q}{2}\left[\frac{1-2Q}{2} + \frac{2}{q}(1-Q)[2(1+Q)]^{\frac{1}{2}}\right]$$

Hence the actual magnitude of the shearing force is independent of the dimensions of the material and the loaded area, and depends only on the load and the value of Poisson's ratio Q for the substance.

Figure 5 shows the value of τ as a function of z/a for value of $Q = 0.5$.

Naturally this solution cannot be applied directly to either the crescent or angle test-pieces, as the stress concentrations complicate the mathematical analysis, but it is significant that in all the practical cases examined the maximum stress occurs in the region of the center of the sample where, as in the simpler case referred to in Figure 5, the stress curve is skew, and the maximum stress occurs nearer the surface. By concentrating the stresses at the base of the crescent or angle the shear stress distribution curve is thus changed from a skew distribution to an almost Gaussian distribution.

DISCUSSION OF THE EFFECT OF DIFFERENT FILLERS IN GR-S, BUTYL, AND NATURAL RUBBER

Comprehensive tear resistance data have been obtained with a range of fillers in the above rubbers, but in the present paper the discussion is centered on points of interest rather than on detailed results.

GR-S

First of all, it is possible to dispose of any argument that direct tears are due to grain effects. It has been found that knotty tears and direct tears occur in samples cut both along and across the grain. A direct tear and a knotty tear can, in fact, occur side by side in the same sample, and this point is illustrated by the samples of GR-S containing 150 parts of Calcene by weight, shown in Figure 6. The explanation of this phenomenon is that the tear proceeds along the direct path first, and as the tear proceeds, so the stress is dissipated. The stress is still concentrated at the base of the nick, and eventually a stage is reached when this stress concentration is sufficiently high to start the knotty tear, and the direct tear stops.

The sample shown in Figure 7 demonstrates how a direct tear can develop into a knotty tear.

BUTYL

The poor tear resistance of compounds containing china clay is well illustrated by the Butyl samples shown in Figure 8, where the discoloration in the region of the tear is due to the rubber being pulled away from the filler. In other words, little reinforcement is imparted by the china clay; the bonds between the filler and the rubber are very weak, and on stretching, the rubber is pulled away from the filler/rubber interface and snaps. It will be noted from close examination of the samples that the tear path is slightly curved at each end. In a previous example[1] the higher permanent set in the region of the start of the tear was taken to illustrate the fact that a higher elongation is necessary to initiate a tear than to propagate a tear. The explanation of the higher permanent set at the end of the tear is provided by Figure 1, where it is shown that in the crescent test-piece the stress passes through a minimum, and as the tear approaches completion, the stress and strain both increase and produce a higher degree of permanent set. This is a very neat, practical confirmation of previous work[12].

Compounds containing whiting also have small forces of cohesion at the rubber/filler interface, and again we find that the rubber is pulled away from the filler. Evidence of this condition is shown by the discoloration of the rubber in the region of the tear in sample 1651 B6, containing 300 parts of whiting by weight, in Figure 9.

Butyl rubber is a very convenient polymer to use in the study of the mechanism of tearing, since it has a high permanent set, which is sensitive enough to show up some of the stress gradients in the sample.

NATURAL RUBBER

Winnofil imparts a high tear resistance to natural rubber[13], and an examination of the samples shown in Figures 10 and 11 leads to several quite important observations. Samples M.680.7 and M.682.11 show very clearly that a maximum shear stress has been developed in a subsurface plane.

With the angle tear test-piece, the higher stress concentrations produce a more marked tongue tear, and the shear stress is more concentrated than with the crescent test-pieces. An actual sample is shown in Figure 12; the shear stress distribution curve is narrower in the case of the angle test-piece, and the maximum shear stress may be greater. The stress concentrations may be too high in the case of the angle test-piece, and the samples in Figure 13 illustrate that in many cases the samples do not tear across the test-piece, but along the line of applied force.

The Calcene samples have the same type of tears as the Winnofil samples, and all the preceding discussion applies equally to Calcene compounds. Several interesting samples showing a maximum shear stress in two planes at right angles were found. With sample M.675.12 (Figure 14) the tear starts, and the line of maximum stress can be seen. After the tear has proceeded about quarter-way across, a direct tear has been initiated, and here again there is evidence of a maximum shear stress. Several samples showing this effect were found, and it may or may not be significant that the double effect was only found in samples tested at elevated temperatures.

With the angle tear specimens the only interesting point is the high preponderance of tears which occur along the line of applied force. These examples certainly show that, in the angle test-piece, the point of tearing is in line with the boundary line of the test-piece, but the stress gradient appears to be too high for compounds containing white fillers.

With zinc oxide samples, examination of the ruptured surfaces of both crescent and angle test-pieces revealed that, although there is evidence of a maximum shear stress being built up in the inner layers, the tongue tears are not deep. In other words, the stress gradient is not steep. Zinc oxide compounds have a higher tear resistance than those containing Winnofil and Calcene, and it is an experimental fact worth noting that as the strength of the material increases, so the frequency with which samples showing evidence of maximum shear stress in subsurface planes are found decreases. This fact is substantiated by the results obtained with black compounds.

The different types of tear found with carbon black stocks of natural rubber were discussed in an earlier publication[1]. In the present discussion only new types are considered.

With the crescent test-piece some Kosmos-20 compounds provided several examples of the serrated-edge type of tear, and sample M.2413.2 shown in Figure 15 is typical. The angle tear specimens are interesting, and in sample M.2413.7A in Figure 16 there are three stress planes. Along the middle plane of maximum stress there are three points where the stress is further intensified and the rubber has been plucked out in the form of solid triangles. In other examples only one triangle was plucked out.

The Magecol samples show the tongue tear typical of a maximum shear

stress in the subsurface planes, and in addition samples M.2409.1A (Figure 17) and M.2409.3A (Figure 18) show a serrated edge tear.

In the case of Kosmobile-HM compounds there is little new to note apart from the fact that only two cases of tongue tears were found with crescent test-pieces. Two examples were also found with the angle test-pieces, and the depth of the tongue was greater, presumably owing to the higher initial stress concentrations. Other examples show the herringbone effect[1], and it should be realized that this is the same as the serrated edge tear, but in the herringbone samples the effect is confined to the surface of the torn edge.

DISCUSSION OF THE CRESCENT AND ANGLE TEST PIECES

In the crescent test-piece a nick 0.02-inch deep is introduced, and the test is really a measure of the propagation of this initial nick. In the angle test-piece, however, the stress is concentrated at the base of the 90-degree angle, and no nick is introduced. The test is, therefore, a combination of tear initiation and tear propagation. The stress is built up at the base of the angle until it is sufficient to initiate a tear, and then further stresses are required to propagate this tear. Using a normal tensile dynamometer, it is only possible to measure the overall force required to rupture the specimen; therefore the force cannot be analyzed into the components producing (1) initiation and (2) propagation.

Even if this separation of forces into components were possible, the interpretation of the results would be difficult, for the distribution of the stresses in these test-pieces is complicated. Therefore, although the angle tear results are generally of a lower order than the crescent tear results (both expressed as kg. per sq. cm.), this point must not be interpreted by itself to mean that the stress required to initiate a tear is less than that for propagation. As Graves[3] has shown, the stress concentrations in the angle test-piece are much higher than in the crescent test-piece, and this condition leads to the recorded forces being lower than those required to tear the crescent test-piece.

In the angle test-piece the point of tearing has been made to correspond with the boundary line of the test-piece instead of with the center line of pull between the boundary lines of the crescent test-piece. This condition increases the stress-gradient, and, as Figure 2 of Graves paper[3] shows, there are several regions of high stress near the apex of the angle. It is sound to argue in favor of a test-piece where the stress at the point of tearing exerts the dominant influence on the tear resistance, but the claim that the angle test-piece meets this requirement cannot be substantiated. In point of fact, the angle test-piece has widely different stress gradients across the width of the test-piece; therefore from the physical point of view the angle test-piece is even more inhomogeneous than the crescent test-piece. If the minimum force required to initiate a tear could be recorded, this objection would be less important, but in the present form of test it cannot be ignored. It has been shown[1] that the different stress distributions in the crescent test-piece produce different types of tearing and lead to more variable results. A powerful objection to any method of intensifying stress heterogeneity in the test-piece is that the difference between straight and knotty tears is increased. This view has been confirmed by the practical results obtained with different fillers in natural rubber. With semireinforcing white fillers, the angle test-piece tends to develop a large number of very pronounced knotty tears. In fact, with most of these samples the tear proceeds along the boundary line of the test-piece in

the direction of pull. As this action occurs with samples cut along and across the grain, it means that with certain compounds the component of stress in the direction of pull is too high. It is significant that, as the strength of the test-piece increases, the frequency of tears in the direction of pull decreases.

The two test-pieces have been compared over a range of volume loadings of different fillers in natural rubber, and an analysis of the different types of tear obtained with the different fillers is given in Table 2.

TABLE 2

COMPARISON OF NUMBER OF STRAIGHT AND KNOTTY TEARS

Filler	Crescent tear		Angle tear	
	Straight	Knotty	Straight	Knotty
Whiting	90	..	90	..
China clay	90	..	90	..
Zinc oxide	..	90	15	75
Calcene	..	90	10	80
Winnofil	..	90	..	90
Kosmos-20	76	14	75	15
Magecol	32	58	30	60
Kosmobile-HM	25	65	63	27

The results fall into three groups. In the first group whiting and china clay, which have low values for tear resistance, do not show knotty tears, and no example of knotty tearing was found with either test-piece. As the resistance to tear increases, however, with the fillers in groups 2 and 3 a large number of knotty tears is found. In the carbon black group Kosmobile-HM and Magecol are found to favor knotty tearing, but Kosmos-20 favors straight tears.

It is interesting that the proportion of straight tears to knotty tears is generally of the same order with both types of test-piece. It should be noted, however, that the angle test-piece usually shows more pronounced knotty tearing when it occurs. There is, therefore, little advantage in either test-piece, since each produces knotty tears, with all the attendant difficulties of interpretation.

Carrying the above analysis a stage further, examination of the individual results and test-pieces showed that the proportion of straight and knotty tears was characteristic of the filler and was reasonably constant for all volume loadings of the filler in natural rubber. This generalization also appears to be true in the case of similar GR-S compounds, but some indications have been obtained with a series of volume loadings of Winnofil in Butyl that, as the proportion of filler is increased, the number of knotty tears increases. These observations are based on results from vulcanizates which were given a cure corresponding to the optimum as determined from tensile strength. It may be that the proportion of straight and knotty tears would be different with under and over cures.

To complete the comparison of the two methods, it is necessary to compare the reproducibility of test results. The coefficients of variation obtained are in general agreement with those published by Morris and Bonnar[5]. The angle method has an average coefficient of variation of 5 per cent, and the crescent method, using the I.C.I. tear cutter, an average coefficient of 6–7 per cent. Although the fact that the angle method has a lower coefficient of variation is important, it must be remembered that the decision as to which is the more

suitable test cannot be based on error considerations alone. The relation of the test to service conditions and the discriminating power of the test are two of the other considerations which must be taken into account. As neither test can be expected to correlate with any one set or all types of service conditions, we need only concern ourselves with discriminating power.

Considering the need of a rest to measure tear initiation, the present author stated in 1945 that it was difficult to see how existing methods for measuring tensile strength could be modified suitably so that the stress to start a tear could be measured. In point of fact, the angle test is only a severe tensile test, and the danger is that it may be too severe. In the earlier investigation[1] results were obtained with the unnicked crescent sample. This test is not so severe as the angle test, yet it gives a measure of tear initiation. If the unnicked crescent were suitable, it would have the added advantage that both initiation and propagation experiments could be carried out on the same test-piece.

To illustrate that the angle test is too severe, the results given in Table 3 have been compiled, and tensile strength, unnicked crescent, crescent tear, and angle tear measurements are compared.

From the table below it is seen that the unnicked crescent results are always intermediate between the normal tensile strength determinations and the standard crescent tear results. This condition is to be expected as the stresses are concentrated in the crescent sample; therefore the unnicked crescent gives lower results than the tensile strength on either rings or dumbbells.

The angle tear results are always lower than the crescent tear results, and are considerably lower than the unnicked crescent. In fact the results in Table 3 show that the stress concentrations in the angle test-piece are too high and that the discriminating power of the test has been reduced too far. There is a wide difference in tensile strength, unnicked crescent tear, and crescent tear of the Winnofil compounds; yet the angle tests give a more or less constant value. For these compounds, therefore, the angle test shows no discriminating power at all.

If it is felt that such a test for tear initiation should be instituted, then the angle test in its present form is too severe. A more hopeful temporary expedient would be to use the unnicked crescent for tear initiation and the nicked crescent for tear propagation. This practice has the great advantage that both tests would be carried out on the same sample. Naturally, it is realized only too well that neither test is wholly satisfactory, but, meantime, until further fundamental work on tear tests is done, this approach seems the best to these difficult problems.

I. G. TEAR CUTTER

This method of preparing ring test-pieces[6] consists of inserting five slits into the inner circumference of a ring at opposite ends of a diameter. In one of the early I.G. models the razor blades were held at the appropriate angle so that all five slits were one millimeter deep and two millimeters apart and were thus arranged radially. In the latest model the razor blades are held vertically and are mounted on a curved holder which has the same curvature as the ring. By going from a radial arrangement of the slits to a vertical one, the I.G. came to the conclusion that the depth of nick is of more importance than the angle at which the nick is introduced. This confirms other work on tear resistance using crescent samples.

TABLE 3

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Tensile strength (kg. per sq. cm.)	253	244	184	157	191	255	264	239	169	171	150	135	118	84	79
Unnicked crescent tear (kg. per sq. cm.)	218	220	180	149	136	223	219	214	127	132	117	109	94	76	68
Crescent tear, 0.02-in. nick (kg. per sq. cm.)	160	111	72	100	50	172	153	162	74	77	72	70	63	54	44
Angle tear (kg. per sq. cm.)	110	62	35	65	30	107	100	101	37	39	39	41	36	36	37

Compound 1 = natural rubber tread.
2 = Neoprene-GN tread.
3 = GR-S tread.
4 = Butyl tread.
5, 6, 7, 8 = increasing loadings of Kosmobile-HM in natural rubber.
9, 10, 11, 12, 13, 14, 15 = increasing loadings of Winnofil in natural rubber.

The results obtained in a preliminary examination of the I.G. tear cutter over a range of natural and synthetic rubbers are compared with crescent and angle tear values in Table 4.

Apart from compounds 1 and 6, the I.G. tear results fall in the same order as the crescent tear results and, in addition, when it is remembered that the I.G. results are expressed as kilograms, they show more discrimination than the angle tear results. The results obtained so far have not been so reproducible as crescent tear results with the same mixes using the I.C.I. tear cutter. Both methods give a measure of tear propagation. In the same way as Poules[14] found that more reproducible results were obtained with the crescent sample when the number of slits was reduced from five to one, it is expected that a corresponding improvement in accuracy could be achieved by inserting only one slit with the I.G. tear cutter. The I.G. used multiple slits in an attempt

TABLE 4

Compound	Crescent tear (kg. per sq. cm.)	I. G. tear (kg.)	Angle tear (kg. per sq. cm.)
1	178	40	110
2	176	51	85
3	165	45	67
4	156	40	83
5	107	33	62
6	107	14	42
7	93	27	65
8	87	23	34
9	83	26	33
10	74	19	35
11	68	21	34
12	63	23	34
13	62	20	38
14	57	13	35
15	48	13	34

Compound 1 = natural rubber tread.
5 = Neoprene tread.
10 = GR-S tread.
7 = Butyl tread.
8, 9, 11, 12, 13, 14, 15 = increasing loadings of Winnofil.
6, 3, 2, 4 = increasing loadings of Kosmobile-HM.

to find any weakness in the material. This method is a novel and interesting one of considering tear tests, but a choice of five or ten slits seems totally inadequate; and if the search for weaknesses is to be followed logically, then slits should be spaced equally round the whole circumference of the ring. At Ludwigshafen the I.G. modified the cutter so that two single slits were placed in the ouside circumference of the ring. We prefer to use a single slit in the outside circumference of the ring, and are in the process of modifying the cutter accordingly. When this work is done, it will be possible to compare the I.G. and crescent methods on a much fairer basis.

CONCLUSIONS

(1) Both the crescent and angle tests are group (2) tests; therefore the width of the sample must be taken into account when the tear resistance is being calculated.

(2) There is one exception to the above, and that is the case of knotty tears in group (2) tests. When knotty tears occur, the test becomes a direct tear test [group (1)], and the width is no longer important.

(3) When knotty tears occur with group (1) tests, the width must be considered for, in reality, the test has become a group (2) test.

(4) Some rubbers exhibit fibering during tearing, and this is explained by the cohesive forces between fibers reaching a limiting value before the limiting value of the breaking strength of a fiber is reached.

(5) Differences in the mechanism of tearing with different fillers have been noted.

(6) Practical evidence of the existence of maximum shear stress in subsurface planes of the material has been obtained, and a mathematical solution for a simple case has been given.

(7) The angle tear method is a combination of tear initiation and tear propagation, and can be regarded as complementary to the crescent test. It cannot be regarded as a replacement for the crescent test.

(8) With certain rubber compounds the component of stress in the direction of pull is too high in the case of the angle test-piece.

(9) It is suggested that the unnicked crescent be used in preference to the angle test-piece for tear initiation measurements, as the unnicked crescent test-piece has more discriminating power.

(10) The same proportion of straight and knotty tears occurs with both the crescent and angle methods.

(11) A preliminary evaluation of the I.G. tear cutter indicates that the fairest comparison with other methods requires a single slit to be inserted in the outside circumference of the ring.

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THE VELOCITY OF PROPAGATION OF ULTRASONIC WAVES AND THE FORM OF THE MOLECULES OF HIGH POLYMERS *

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In earlier and what was preliminary work[1], the present authors observed that the velocity of propagation of ultrasonic waves in liquids of high molecular weight or in solutions depends on the form of the molecule and particularly on the frequency and length of side chains. It was also observed, in a study of a series of hydrocarbons and of certain polyethers, that the ratio of the velocity of propagation and the density of homologous polymers increases with increase in the molecular weight of chain compounds with no side chains or with but few side chains, that the ratio remains practically constant for compounds containing closely spaced side methyl or ethyl groups, and that it decreases with increase in the molecular weight of compounds containing closely spaced side groups of larger size.

In addition it was found in the earlier work that, in the case of substances of low molecular weight, the adiabatic compressibility depends on the form of the molecule.

The velocity of propagation u of ultrasonic waves in a liquid is related to the adiabatic compressibility β and to the density ρ by the known equation:

$$u = \sqrt{\frac{1}{\rho\beta}}$$

As has been shown by one of the present authors[2], the adiabatic compressibility for various series of liquid isomers of low molecular weight is related directly to the molecular structure, provided that the isomers are at the particular temperatures at which their densities are the same. Under such conditions, for example, the greater the number of side chains in the molecules of the nine isomeric heptanes, the greater is their adiabatic compressibility, and various isomeric ethylenes are more compressible in the *cis*-form than in the *trans*-form.

Other authors, for example, Frenkel[3], had assumed previously from other considerations that the molecules of a liquid are not to be regarded as "rigid", but rather as appreciably compressible. Furthermore, the variations in the molecular refraction observed in some gases at high pressures, *e.g.*, carbon dioxide, have been explained by De Groot and Seldam[4] as the effect of variations in the molecular radius as a function of the pressure. In view of these hypotheses we could only conclude that the spatial structure influences the compressibility.

We have now extended the study to numerous substances of high molecular

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weight, and have been able to establish a clearer dependence between the velocity of the propagation of ultrasonic waves on the form of the molecule by comparing experimental velocities with those which can be theoretically predicted by empirical formulas already known and fairly well verified for compounds of low molecular weight.

As we shall see later, we have defined as the *form factor* the ratio between the experimental velocity and the calculated velocity, because this ratio has been found to be related to the form of the molecule.

Let us examine how this definition of the form factor was derived.

According to Rao[5], the velocity of propagation of ultrasonic waves in an unassociated liquid can be calculated on the basis of the nature of the atoms which make up the molecule by means of the empirical relation which he established between the cube root of this velocity u and the molecular volume:

$$\sqrt[3]{u} \cdot \frac{M}{\rho} = R = \sum m R_i$$

where M is the molecular weight and ρ is the density. R is independent of the temperature for every unassociated liquid, and appears as an additive constant. It can, in fact, be calculated as the sum of the partial constants R_i, each one relating to every atom contained m_i times in the molecule, or better, can be referred to the different valence bonds present in the molecule. Obtaining thus the value of R, the value of u at any temperature can be calculated from the above equation by introducing for ρ the value of the density at the same temperature. If the law of additivity assumed by Rao for the R constants, based on the partial R_i values relative to the individual atoms composing the molecule, were strictly valid, it would obviously be incompatible with the dependence, already demonstrated by us, of the velocity of propagation of ultrasonic waves on the structure of the molecule of various series of isomers. In fact, on the basis of the formula of Rao, the velocities of propagation in various isomers at the same temperature would have to be proportional to the third power of the density, and this does not agree with facts, as is evident when one considers, for example, such a case as the isomeric heptanes mentioned above.

Lagemann and Corry[6] have proposed to calculate the R constants, not as the sum of the constants relating to the single atoms, but rather as the sum of the values corresponding to the various bonds contained in the molecule, and have thus introduced the concept of "bond velocity".

The values proposed by Lagemann and Corry for the bonds which are involved in the products studied in the present work are given below:

C—H	95.2	O—H	99.0
C—C	4.25	C—C	129
C—O	34.5	C—O	186

Such a method of calculation should give, according to the authors, results which would appear to be in better accord with experimental data than were those of Rao. Nevertheless, even this method necessarily disregards the influence on the velocity of propagation of the form of the molecule when isomers containing the same chemical bonds or *cis-* and *trans-*isomers are involved.

We propose, therefore, to introduce a definite form factor for every liquid compound as the ratio of the velocity of propagation found experimentally at

a definite temperature to the calculated velocity of propagation at the same temperature, based on the atoms or on the component chemical bonds and on the relation:

$$u = \left(\frac{R_\rho}{M}\right)^3$$

The form factor is found to be independent of the temperature.

The velocity of propagation of the ultrasonic waves was measured by the method of Hiedemann, which is applicable only to transparent substances and to the liquid state. The same method was also used for substances which are solid at ordinary temperature. When the substances melted at temperatures below 100°, the measurements were made at different temperatures above those of the melting points. On the other hand, in the case of substances fusible with difficulty or which were extremely viscous even at a high temperature (the coefficient of absorption of the ultrasonic waves is proportional to the coefficient of viscosity), various measurements were made on solutions close to the point of saturation and also on solutions of lower concentration. In such a case the velocity of propagation as determined experimentally was assumed to be that obtained by extrapolation of the velocities of propagation of solutions of increasing concentrations to a concentration of solute of 100 per cent, and introducing, to calculate the velocity of propagation by the formula of Rao, the density for the hypothetical superfused liquid state deduced in a similar way from the densities of the solutions.

Such extrapolations give values which are in satisfactory agreement, even in the case of limited solubility, only when the solutions conform approximately to the laws of additivity of specific volumes, or when ideal solutions are involved; in such a case, in fact, while the density ρ_c of the mixture appears to be a linear function of the concentration by volume c, the velocity of propagation u_c, as has been already shown by the present authors[7], can be expressed by the formula:

$$u_c = \frac{1}{\frac{c}{u_1} + \frac{1-c}{u_2}}$$

where u_1 and u_2 are the velocities of propagation in the two pure components, or rather if it is desired to refer to the concentration by weight x, by the formula:

$$u_x = \frac{1}{\left(\frac{x}{u_1\rho_1} + \frac{1-x}{u_2\rho_2}\right)\rho_x}$$

where u_1 and u_2 are the densities of the pure components in the liquid state; u_x and ρ_x are the velocities of propagation and density of the mixture of concentration x, respectively.

Either of these two equations can be solved with respect to the unknown u_1 (velocity of propagation determined experimentally in the solid considered as in the superfused liquid state) when the values of all the other factors contained in the equation are known.

$$u_1 = \frac{c}{\frac{1}{u_c} - \frac{1-c}{u_2}} = \frac{x}{\left(\frac{1}{u_x\rho_x} - \frac{1-x}{u_2\rho_2}\right)\rho_1}$$

The value of $\rho_1 = \frac{\rho_c - \rho_2(1 - c)}{c}$ is also introduced into the formula of Rao for the calculation of the theoretical velocity of propagation expressed as $u = \left(\frac{R}{M}\rho_1\right)^3$ in all those cases in which direct measurement of the density of the polymer in the liquid state is not possible. The values of the densities of the products calculated in this way are affected by errors the magnitudes of which are greater the less the concentration of the solute and the greater the deviation of the solution from the ideal.

As far as substances of low molecular weight are concerned, the influence of the molecular structure on the form factor is evident by an examination of Table I, which gives the velocities of propagation of the nine isomeric heptanes

TABLE I

Hydrocarbon	Experimental u at 20° C (Freyer, Hubbard and Andrews) (m. sec.$^{-1}$)	Calculated u at 20° C (Rao) (m. sec.$^{-1}$)	Form factor
n-Heptane	1154	1170	0.985
2-Methylhexane	1120	1158	0.965
3-Methylhexane	1135	1205	0.940
3-Ethylpentane	1169	1260	0.925
2,2-Dimethylpentane	1080	1123	0.960
2,3-Dimethylpentane	1148	1238	0.931
2,4-Dimethylpentane	1083	1143	0.947
3,3-Dimethylpentane	1129	1234	0.913
2,2,3-Trimethylbutane	1101	1225	0.900

already determined at 20° C by Freyer, Hubbard and Andrews[8], the velocities calculated by the equation of Rao, on the basis of the values of the bond velocities of Lagemann and Corry, and finally the form factors derived from them.

An examination of Table I makes it evident that the form factor decreases with increase in the length and number of side chains and with increase in the symmetry of the molecule.

A detailed examination of these factors for substances of low molecular weight will be the object of a further paper. In the present work we wish to refer to the results already obtained in the determination of the form factor of substances of high molecular weight.

It should be noted in the first place that, if the law of Rao holds true, the velocity of propagation of the ultrasonic waves for members of a series of homologous polymers ought to be proportional to the cube of the density and be independent of the molecular weight.

In fact, if n is the degree of polymerization, m is the weight of the base molecule, and r the relative constant of Rao, then for degrees of polymerization which are sufficiently high to reduce the influence of the terminal groups:

$$M = n \cdot m \qquad R = n \cdot r \qquad u = \frac{R^3}{M^3}\rho^3 = \left(\frac{r}{m}\right)^3\rho^3 = K\rho^3$$

For very high molecular weights, ρ also tends toward a constant limiting value, and the same should be true for the velocity of propagation.

Consequently, the form factor, which is the ratio of the two velocities of propagation, also should tend, at sufficiently high molecular weights, toward a

limiting value which is independent of the molecular weight and therefore is dependent only on the form of the molecule. The experimental results which the present authors have already obtained confirm these deductions, as will be seen later.

The method proposed, notwithstanding the low stability of the large molecules with respect to ultrasonic waves recently pointed out by Mark[9], can be applied to the study of substances of high molecular weight because it is possible to avoid practically any appreciable depolymerization by using an apparatus of small power and reducing the time necessary for carrying out the measurements.

EXPERIMENTAL PART

The results so far obtained in determining the velocity of propagation of ultrasonic waves in different series of high polymers, both in the fused state and in solution, and in the calculation of their respective form factors, will now be explained.

The experimental determination of the velocity of propagation was carried out with the method of Bache, Heidemann and Asbach[10], as modified by Giacomini, and described in an earlier work[11].

The high-frequency oscillator (4MHz) was designed and constructed at the National Institute of Electro-Acoustics of the National Council of Research (l'Istituto Nazionale di Elettroacustica del Consiglio Nazionale delle Ricerche).

For the products in the liquid state which were examined at temperatures other than room temperature and for solutions, the approximation of the measurements can be controlled within ± 2 meters per second; the values of the extrapolated velocities for the solutes are, on the other hand, subject to greater errors, particularly in cases where it is necessary to carry out measurements on solutions of low concentration and on solutions which are extremely viscous or are not transparent.

The experimental velocities were compared with the calculated velocities, using the values of the "bond velocity" proposed by Lagemann and Corry; for the bonds C—N and N—H, which were not studied by Lagemann and Corry, we carried out corresponding determinations with carefully chosen compounds.

The densities of the solutions and of the fused products which were not very viscous were determined by means of a Westphal balance with a cylinder, heat-controlled to within $\pm 0.1°$ C; the densities of the highly viscous products were determined by means of a volumometer.

HYDROCARBONS OF HIGH MOLECULAR WEIGHT

In this group three hydrocarbons were examined: an ordinary grade of paraffin with a melting point of 60° C, a paraffin obtained with the Fischer-Tropsch process having a melting point of 90° C, and polyethylene from the Imperial Chemical Industries.

The first two products were examined in the fused state, the third was examined in a hot xylene solution and in a solution in paraffin having a melting point of 60° C, likewise at elevated temperature.

In Table II are reported the velocities of propagation of the ultrasonic waves and the experimental densities at various temperatures of the liquids examined, as well as the velocities of propagation that were calculated for polyethylene in the superfused state by extrapolating the values of the solutions

in xylene or in paraffin, on the assumption that these solutions are ideal. The densities of the solutions of polyethylene in xylene are obviously equal to those of the pure solvent, which shows that, at the temperatures at which the experiments were carried out, the polyethylene in solution had practically the same density as the solvent.

In the same table are also recorded, for the three products examined, the velocities of propagation, calculated by the method described, which is based on the equation of Rao and the relative form factors: $f = \frac{u \text{ exptl.}}{u \text{ calcd.}}$

For all three of the products examined, these latter are close to unity, and, as was foreseen, do not vary appreciably with changes in temperature.

TABLE II

Substance	°C (±0.1°)	Experimental u (m. sec.$^{-1}$)	ρ (g. per cc.)	Calculated u (m. sec.$^{-1}$)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Paraffin with melting point	60.0	1293	0.781±0.001	1278	1.01
	70.0	1261	0.776±0.001	1250	1.01
	95.0	1179	0.763±0.001	1193	0.99
	99.0	1165	0.761±0.001	1179	0.99
Paraffin (Fischer) (m.p. 90° C)	98.0	1224	0.764±0.001	1196	1.01
	100.3	1217	0.763±0.001	1190	1.01
Solutions of polyethylene:					
(1) Xylene solutions (5.52% by wt.)	75.0	1129	0.819±0.001	—	—
	80.0	1107	0.815±0.001	—	—
(2) Xylene	20.0	1340	0.865±0.0002	—	—
	75.0	1107	0.819±0.001	—	—
	80.0	1087	0.815±0.001	—	—
(3) Solution in paraffin (m.p. 60° C) (5.87% by wt.)	95.0	1189	0.765±0.001	—	—
	99.0	1175	0.763±0.001	—	—
(4) Polyethylene in xylene in paraffin	75.0	1480	0.819±0.010*	1472	1.00
	80.0	1450	0.815±0.010*	1750	1.00
	95.0	1420	0.804±0.010*	1395	1.02
	99.0	1380	0.800±0.010*	1372	1.01

* Values of the density in the superfused state calculated from the density of the solutions in xylene assumed to be ideal.

In addition, there were examined not only a triisobutylene which the present authors prepared, but also a series of polyisobutylenes (Oppanol-B of the I-G. Farbenindustrie) of different molecular weights (3000, 6000, 15,000 and 200,000), a sample of Butyl rubber (isobutylene copolymerized with 1–2 per cent of isoprene), a polymer of α-butylene prepared in the laboratory of the present authors, and a copolymer obtained from a mixture of 79 per cent of α-butylene and 21 per cent of butadiene by the action of aluminum chloride. The relative results are reported in Table III.

Of these products we were able to examine directly the first and the last two at more or less elevated temperatures; the polyisobutylenes with higher degrees of polymerization were examined in a solution in normal heptane at 20° C, and the Butyl rubber was examined in solution in cyclohexane.

The form factors of the polyisobutylenes were practically independent of the molecular weight, and equal to 0.80; the form factor of Butyl rubber (dissolved in cyclohexane) was 0.65. The polymer of α-butylene showed a form

TABLE III

Substance	Temp. °C (±0.1°)	Experimental u (m. sec.$^{-1}$)	ρ (g. per cc.)	Calculated u (m. sec.$^{-1}$)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Triisobutylene	20	1237±1	0.759 ±0.001	1360	0.91
Polyisobutylene (mol. wt. 3000)	65	1350±2	0.860 ±0.001	1700	0.80
Polyisobutylene (mol. wt. 6000) in heptane (10.80% by wt.)	20	1173±2	0.704 ±0.001	—	—
Heptane	20	1153±1	0.6834±0.0002	1170	0.985
Polyisobutylene (mol. wt. 6000)	20	1460±10	0.884 ±0.002	1853	0.79
Polyisobutylene (mol. wt. 15000) in heptane (14.0% by wt.)	20	1180±2	0.709 ±0.001	—	—
Polyisobutylene (mol. wt. 15000)	20	1485±10	0.892 ±0.002	1900	0.79
Polyisobutylene (mol. wt. 200,000) in heptane (5.10% by wt.)	20	1171±2	0.693 ±0.001	—	—
Polyisobutylene (mol. wt. 200,000)	20	1848±25	0.953 ±0.010*	2318	0.80
Butyl rubber in cyclohexane (5.57% by wt.)	20	1286±2	0.784 ±0.001	—	—
Cyclohexane	20	1281±1	0.777 ±0.0002	1259	0.01
Butyl rubber	20	1395±10	0.930 ±0.005*	2152	0.65
Poly-α-butylene	45	1320±2	0.842 ±0.001	1620	0.82
	50	1306±2	0.840 ±0.001	1600	0.82
	55	1291±2	0.837 ±0.001	1575	0.82
Copolymer of 79% α-butylene and 21% butadiene	80	1238±2	0.846 ±0.001	1630	0.76
Polystyrene in styrene (6.50% by wt.)	20	1364±2	0.898 ±0.001	—	—
Styrene (monomer)	20	1354±1	0.887 ±0.001	1360	1.00
Polystyrene in benzene (19.88% by wt.)	20	1346±2	0.913 ±0.001	—	—
Benzene	20	1323±1	0.879 ±0.001	1310	1.01
	30	1275±1	0.869 ±0.001	1265	1.01
Polystyrene in styrene	20	1524±25	1.093 ±0.020*	1832	0.83
Polystyrene in benzene	20	1470±10	1.093 ±0.005*	1790	0.82

* Values of the density in the superfused state calculated from assumed ideal solutions.

factor of 0.82, and the form factor of the copolymer with butadiene was lower, *viz.*, 0.76.

Table III also gives data on solutions of a polystyrene obtained by spontaneous polymerization of the monomer in styrene and in benzene at ordinary temperature, and the corresponding form factor, which was calculated as 0.82–0.83.

In further experiments, samples of natural rubber and masticated rubber, a sample of Buna-32, and another sample of Buna-32 completely hydrogenated in our laboratory, were examined. All the products were examined in normal heptane solutions at 20° C except the natural rubber, which was examined at elevated temperature in solution in paraffin having a melting point of 60° C. The results are reported in Table IV.

The value of the form factor is 0.89–0.90 for natural rubber; 0.80 for rubber masticated 10 minutes, and 0.82–0.94 for Buna-32, whether hydrogenated or not.

TABLE IV

Substance	Temp. °C (±0.1°)	Experimental u (m. sec.$^{-1}$)	ρ (g. per cc.)	Calculated u (m. sec.$^{-1}$)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Natural rubber in paraffin (melting point 60° C) (see Table II)					
(7.43% by wt.)	70	1273±2	0.783±0.001	—	—
	75	1256±2	0.780±0.001	—	—
Natural rubber	70	1465±20	0.880±0.010*	1635	0.90
	75	1435±20	0.876±0.010*	1610	0.89
Masticated rubber in heptane (see Table III) (6.64% by wt.)	20	1166±2	0.696±0.001	—	—
Rubber masticated 10 minutes	20	1387±20	0.904±0.010*	1730	0.80
Buna-32 in heptane (11.45% by wt.)	20	1170±2	0.708±0.001	—	—
Buna-32	20	1435±10	0.906±0.002**	1710	0.84
Hydrogenated Buna-32 in heptane (20.60% by wt.)	20	1200±2	0.717±0.001*	—	—
Hydrogenated Buna-32	20	1530±10	0.885±0.002**	1870	0.82

* Density values in the superfused state calculated from the density of assumed ideal solutions.
** Values calculated by extrapolations from determinations at higher temperatures.

The comparison between the form factors of the hydrocarbons of high molecular weight with those of hydrocarbons of analogous constitution but of low molecular weight is of particular interest.

In this connection Table V shows, both for compounds of low molecular weight and for those of high molecular weight which were examined, the form factors in relation to the ratio ψ between the number of side chains and the number of atoms in the principal chain.

An examination of Table V shows that, both with products of high molecular weight and with those of low molecular weight, the more frequent and the

TABLE V

Hydrocarbons of low molecular weight				Hydrocarbons of high molecular weight			
Substance	ψ	Type of side chains	f	Substance	ψ	Type of side chains	f
Normal heptane	0	—	0.985	Normal paraffins and polyethylene	0	—	1.00
Methylhexanes (2- and 3-)	0.167	CH_3	0.952	Natural rubber	0.25	CH_3	0.90
Ethylpentane	0.2	C_2H_5	0.925	Poly-α-butylenes	0.5	C_2H_5	0.82
Dimethylpentanes (2,2-; 2,3-; 2,4-; 3,3-)	0.4	CH_3	0.937	Polystyrenes	0.5	C_6H_5	0.82
Trimethylbutane	0.75	CH_3	0.900	Polyisobutylenes	1	CH_3	0.80

more extensive are the side chains, the smaller is the form factor; and furthermore that, for products of high molecular weight, the influence of the side chains of the molecules is somewhat more sensitive than in products of low molecular weight.

The effect of the side chains of the molecule on the form factor is evident also from conclusions which can be drawn from the results in the preceding tables. Thus the lowest value of f (0.76) shown by the copolymer obtained from a mixture of 79 per cent of α-butylene and 21 per cent of butadiene, both in comparison with the polymer of α-butylene (see Table III) and in com-

parison with Buna (see Table IV), is explained by the formation of bridges and consequent increase in the degree of branching of the molecules. It should be noted also that this effect is even more marked in Butyl rubber (copolymer of isobutylene with 1–2 per cent of isoprene), which has a form factor of 0.65 (see Table III).

The lowest form factor of rubber masticated for 10 minutes (0.80) in comparison with that of natural rubber (see Table IV) can be explained on the basis of the hypothesis advanced by Staudinger[12], according to which not only does depolymerization occur during mastication, but the form of the molecules changes in the sense of more extensive branching by formation of oxygen bridges.

The data in Table IV also give further confirmation that the polymerization of butadiene to Buna does not take place, at least not mainly, in the 1,4-position; in fact the values of f for Buna and for the product obtained by the hydrogenation of this same Buna are equal to 0.82–0.84, *i.e.*, equal to the form factor found for the polymers of α-butylene, which is but slightly different from the form factors of polyisobutylene; this polymerization must, therefore, take place for the most part either in 1,2-position or in 2,3-position. This is in agreement also with the recent results of Homson and Halverson[13], which are derived from the roentgenographic examination of samples of Buna stretched at a low temperature.

POLYVINYL ESTERS AND POLYVINYL ETHERS

With a view to a more thorough study of chain compounds with branchings and in some cases where these side chains in turn contain branchings, a sample of polymethyl acrylate, a sample of polymethyl methacrylate, and a sample of polyvinyl isobutylene ether (Oppanol-C of the I.-G. Farbenindustrie) were examined. These products were examined in solutions of methylene chloride, of benzene, and of carbon disulfide at room temperature. The results are summarized in Table VI, which also contains data on monomeric methyl methacrylate.

The form factor, which is close to 1 for the monomers, is 0.89 for polymethyl

TABLE VI

Substance	Temp. °C (±0.1°)	Experimental u (m. sec.$^{-1}$)	ρ (g. per cc.)	Calculated u (m. sec.$^{-1}$)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Polymethacrylate in methylene chloride (5.20% by wt.)	30	1058±2	1.305 ±0.001	—	—
Methylene chloride	30	1050±2	1.312 ±0.001	—	—
Polymethacrylate	20	1257±20	1.150 ±0.010*	1408	0.89
Methyl methacrylate (monomer)	30	1175±2	0.929 ±0.001	1227	0.96
	40	1132±2	0.918 ±0.001	1184	0.96
Polymethyl methacrylate in acetone (5.13% by wt.)	20	1197±2	0.820 ±0.001	—	—
Acetone	20	1192±1	0.7927±0.0002	1158	1.03
Polymethyl methacrylate	20	1265±20	1.220 ±0.010*	2008	0.62
Polyisobutyl ether in carbon disulfide (4.01% by wt.)	20	1157±2	1.246 ±0.001	—	—
Carbon disulfide	20	1157±1	1.264 ±0.001	—	—
Polyvinylisobutyl ether	20	1160±20	0.925 ±0.010*	1470	0.78

* Data obtained from solutions assumed to be ideal.

acrylate and 0.63 for polymethyl methacrylate; the latter has two side chains for every two atoms of carbon in the main chain. The form factor of polyvinylisobutyl ether is also low (0.78), and this compound contains for every two carbon atoms in the main chain, a side chain which is, in its turn, branched.

POLYOXYMETHYLENES, POLYETHYLENE OXIDES, AND POLYAMIDES

Finally a polyoxymethylene obtained by spontaneous polymerization at room temperature of concentrated aqueous solutions of formaldehyde free of methanol, a polyethylene oxide obtained likewise by spontaneous polymerization of the monomer at room temperature, and a sample of Nylon 6–6, were examined. The first two products were examined in ethyleneglycol solution, the third in formic acid solution.

In addition, a sample of caprolactam was examined in the fused state[14] with the object of calculating the form factor for Nylon, since the part played by the C—N and N—H bonds in the constant R of Rao was not calculated by Lagemann and Corry[6].

At a temperature of 70° C, fused caprolactam showed a u value of 1450 and a ρ value of 1.022; at 80° C a u value of 1418 and a ρ value of 1.017. From the mean value of $R = \frac{\sqrt[3]{u}}{\rho} M$ calculated from such data (1250) and from the summation of R relative to the remaining bonds constituting the molecule of caprolactam (1159) calculated on the basis of the values of Lagemann and Corry, the value of 91 was derived, corresponding to two C—N bonds and to one N—H bond.

In the case of polyethylene oxide and of Nylon 6–6, the form factors are close to unity, which is in accord with an absence of branchings in their molecules. The results obtained with solutions of polyoxymethylene in glycol are not reported, but polyoxymethylene has a form factor greater than unity, because the viscosities of the solutions are irregular, and it is suspected that a reaction between solvent and solute, with possible formation of acetals, may have taken place.

In Table VII, which has been compiled by the same methods used for Table V, the data given in Tables VI and VII are compared with the form factors of products of similar structure and of low molecular weight.

In these cases too, the form factors of products of low molecular weight, although indicating a slight dependence on the side chains of the molecule,

TABLE VII

Substance	Temp. °C (±0.1°)	Experimental u (m. sec.$^{-1}$)	ρ (g. per cc.)	Calculated u (m. sec.$^{-1}$)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Polyethylene oxide in ethylene glycol (11.18% by wt.)	40	1614±2	1.102±0.001	—	—
	50	1590±2	1.094±0.001	—	—
Ethylene glycol	20	1667±2	1.112±0.001	1602	1.04
	40	1619±2	1.099±0.001	1545	1.05
	50	1594±2	1.092±0.001	1497	1.06
Polyethylene oxide	40	1565±10	1.117±0.005*	1534	1.02
	50	1560±10	1.110±0.005*	1502	1.04
Nylon 6–6 in formic acid (6.66% by wt.)	30	1379±2	1.168±0.001	—	—
Formic acid (~80%)	30	1355±2	1.175±0.001	—	—
Nylon 6–6	30	1710±20	1.085±0.010*	1735	1.00

* Data calculated from solutions assumed to be ideal.

TABLE VIII

Esters and ethers of low molecular weight			
Substance	ψ	Type of side chains	f
Ethyl ether	0	—	1.02
Methyl acetate	0	—	1.02
Methyl propionate	0	—	0.98
Isobutyl acetate	0.167	CH_3	0.98
Methyl isobutyrate	0.167	CH_3	0.97
Methyl methacrylate (monomer)	0.2	CH_3	0.96

Polyesters and polyethers			
Substance	ψ	Type of side chains	f
Polyethylene oxide	0	—	1.03
Methyl polyacrylate	0.5	$CO—O—CH_3$	0.8
Polyvinylisobutyl ether	0.5	$O—CH_2—CH(CH_3)_2$	0.78
Methyl polymethacrylate	1	CH_3 $CO—O—CH_3$	— 0.63

do not deviate more than a few per cent from unity, whereas products of high molecular weight show f values which are lower than those of compounds with branched chains. A comparison of these values themselves with those given in Table V confirms the dependence of the form factors of the high polymers on the frequency of the branchings, on the length of the latter, and, finally, on the secondary branchings.

In conclusion, the results of the determinations of ultrasonic wave velocities in substances of high molecular weight, where the concept of the form factor, defined as the ratio between the experimental velocity and the calculated velocity, is introduced, make it possible to draw important deductions concerning the degree of branching of the molecules of high polymers. It appears, therefore, that this method can be applied, in addition to the other methods previously mentioned, to the study of natural and synthetic products of high molecular weight.

SUMMARY

The velocity of propagation of ultrasonic waves in numerous substances of high molecular weight was determined. For substances not fusible at temperatures below 100° C, this velocity was determined by extrapolation from solutions considered ideal.

For linear macromolecules without side chains, the ultrasonic velocity appears to be practically equal, within the limits of experimental error, to that calculated by the formula of Rao and on a basis of the additive values of the bond velocity of Lagemann and Corry.

For molecules which have many side chains, the velocity is lower than the calculated value, whereas for compounds of low molecular weight this deviation is relatively small, *viz.*, less than 10 per cent; it becomes much higher, *viz.*, almost up to 40 per cent, for macromolecules.

The form factor is defined as the ratio of the velocity determined experimentally to the velocity calculated by the formula of Rao. This form factor is equal to 1 for polymers without side chains or with very few side chains, such as paraffins, polyethylenes, Nylon, polyethylene oxides, and polyoxymethylenes; is only 0.89–0.90 for natural rubber; only 0.82–0.84 for Buna and for hydrogenated Buna, poly-α-butylenes, and polystyrenes; only 0.79–0.80 for polyisobutylenes; only 0.89 for polymethacrylates; only 0.78 for polyvinylisobutyl ethers; only 0.65 for Butyl rubber; and only 0.63 for polymethyl methacrylates.

The form factor is thus affected by the frequency and length of the side chains, and by any secondary side chains which may be present.

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[14] The following values were obtained at 20.0° ± 0.1° C. Methyl acetate: u = 1183 ± 1 m. per sec.; ρ = 0.937 ± 0.001 g. per cc. Methyl propionate: u = 1173 ± 1 m. per sec.; ρ = 0.909. Isobutyl acetate: u = 1178 m. per sec.; ρ = 0.870. Methyl isobutyrate: u = 1163 m. per sec.; ρ = 0.890. For ethyl ether, the values of Freyer, Hubbard, and Andrews (*J. Am. Chem. Soc.* **51**, 759 (1929)) and reported by Hiedemann ("Ultraschallforschung", de Gryter ,Berlin, **1939**, p. 227) were accepted.

PROPAGATION OF AUDIOFREQUENCY SOUND IN HIGH POLYMERS *

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INTRODUCTION

The evaluation of the dynamic viscoelastic properties of a material can be made from measurements of the velocity of transmission and the attenuation of sound in the material. Such methods have been applied chiefly to "low loss" materials, such as metals, and to some plastics by Mason, McSkimin, *et al.* A standing wave method for measurement of the dynamic modulus in thin strips was suggested by Bridgeman and Trueblood, and was applied by Ballou and Silverman[1] to the measurement of Young's modulus in low-loss materials. A modification of this technique can be extended to measure also the internal friction of high-loss materials. By this method, Nolle[2] obtained the viscoelastic constants of some high polymers. Independently, a method similar to that employed by Nolle has been used in the present work[3].

The experimental procedure may be best understood by reference to the block diagram shown in Figure 1. The signal generator drives a crystal,

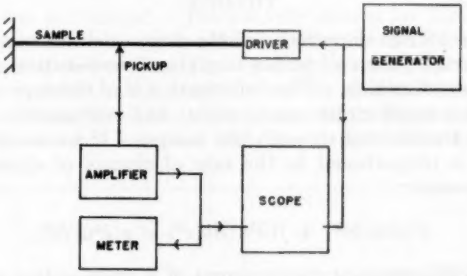

Fig. 1.—Schematic diagram of experimental method.

setting up longitudinal waves which are transmitted through the sample and picked up by a reluctance or crystal receiving element. The received signal is amplified and fed to one set of oscilloscope plates; the other set is connected directly to the driving oscillator. Thus, the phase difference between the driven end and the pick-up can be ascertained for any point along the sample. By moving the pick-up along the sample, the distance between two adjacent points in the same phase of motion can be measured, and thus the wave length of the sonic wave in the sample can be determined. Knowing the frequency of the driving oscillator, the velocity can be directly obtained.

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The attenuation is obtained by moving the pick-up along the sample and reading on the wave analyzer, or sound level meter, the amplitude of the received signal as a function of distance.

This method of measurement is limited to a definite frequency range, and is applicable only to certain materials. An upper limit to the frequency range is determined by the fact that the largest cross-sectional dimension of the sample must be kept small in comparison with the wave length of the propagated wave. At sufficiently low frequencies, the sample length becomes smaller than the half-wave length of the transmitted sound wave, making velocity measurements impossible. Besides these limitations, it is also evident that materials of extremely high attenuation cannot be investigated by this method because of the rapid decay of the transmitted wave. Conversely, measurements of materials having very small attenuation are complicated by reflections which tend to produce standing waves and thus give rise to spurious attenuation readings. The samples used in the present investigation were thin strips 0.45 mm. thick and 2–3 mm. wide. The cross-section was thus a very small fraction of the wave lengths used. The length of the strips was of the order of 20–30 cm., and the damping was sufficiently high to prevent standing waves due to reflections from the end of the sample. This length of sample also made it possible to measure the wave length and attenuation over a considerable distance, and thus to increase the accuracy of the measurements. The velocity could be measured to an estimated precision of 0.4 per cent. The attenuation measurements, particularly those at the higher frequencies, could not be obtained to better than 10 per cent, due to the rapid rise in absorption with frequency. This confined the measurements to a small portion of the sample.

THEORY

If the cross-sectional dimensions of the strip used are small in comparison with the wave length, then all points in a given cross-section are, presumably, in the same phase of motion. The deformation is of the type encountered in a Young's modulus stress-strain relationship, and acoustically, a plane longitudinal wave is transmitted through the sample. If we assume also that the frictional force is proportional to the rate of change of strain, the following wave equation results:

$$E(\partial^2 u/\partial x^2) + f(\partial^3 u/\partial t dx^2) = \rho(\partial^2 u/\partial t^2), \tag{1}$$

where u is the instantaneous displacement of a cross-section of the sample in the x direction; E is Young's modulus, f the viscosity coefficient, and ρ the density of the material. Assuming a sinusoidal driving force, a solution of the equation yields the following relationships:

$$E = \rho C^2 \frac{\omega^2(\omega^2 - \alpha^2 C^2)}{(\omega^2 + \alpha^2 C^2)^2} \tag{2}$$

and

$$f = \rho C^2 \frac{2\omega^2 \alpha C}{(\omega^2 + \alpha^2 C^2)^2}, \tag{3}$$

where ω is the angular frequency and C the phase velocity of the transmitted wave. These equations relate the normal viscosity coefficient f and the dynamic Young's modulus E with the measurable quantities.

EXPERIMENTAL RESULTS

Figure 2 shows the velocity curves for a Butyl gum stock as a function of frequency at different temperatures. The velocity increases very slowly with frequency at high temperatures where the values of the velocity are of the order of 40 meters per second. The increase in velocity with frequency is much more rapid as the temperature is lowered, and the velocity at 0° C is of the

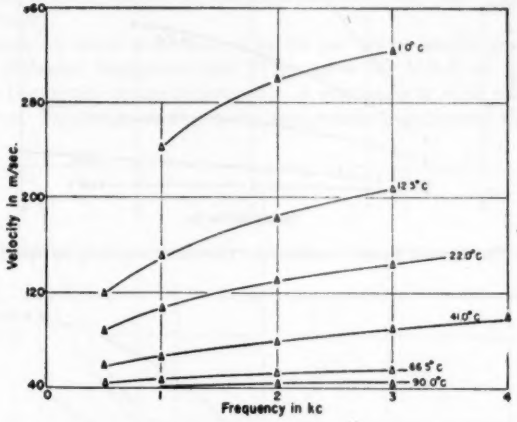

FIG. 2.—Velocity *vs.* frequency for a Butyl gum stock.

order of 300 meters per second. The velocity curves for GR-S are shown in Figure 3. The general behavior is similar to that in Butyl, but the velocity in GR-S is in general lower than that of Butyl at a given temperature and frequency. The corresponding modulus curves derived from the velocity curves, using Equations (2) and (3), are presented in Figures 4 and 5. At all temperatures the modulus increases with frequency. This increase is much

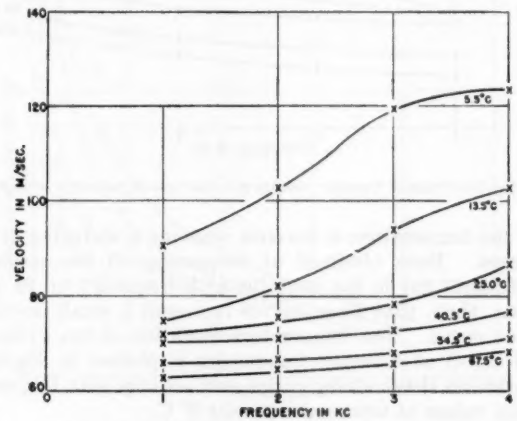

FIG. 3.—Velocity *vs.* frequency for a GR-S gum stock.

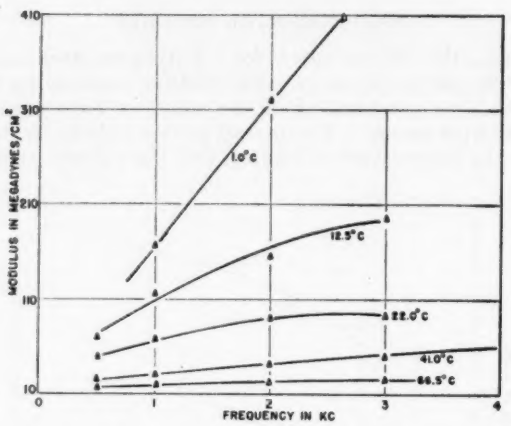

FIG. 4.—The dynamic Young's modulus as a function of frequency for Butyl gum.

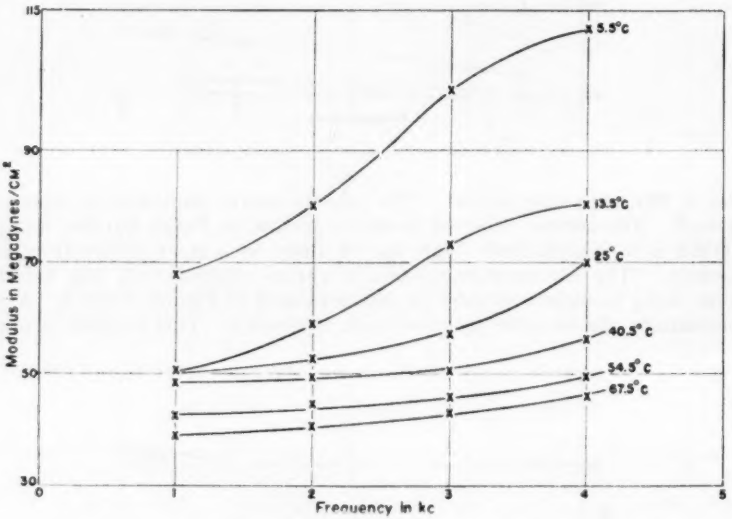

FIG. 5.—The dynamic Young's modulus as a function of frequency for GR-S.

more rapid as the temperature is lowered, showing a stiffening of the stock at low temperatures. Data obtained at frequencies in the megacycle range[4] indicate a continuous rise in the modulus with frequency up to 10 or 15 Mc. It would appear, then, that these curves represent a small portion of a very broad dispersion curve. The temperature variation of the dynamic modulus for Butyl and GR-S at different frequencies is plotted in Figures 6 and 7. At high temperatures the modulus varies only slightly with frequency, but has widely divergent values at temperatures near 0° C.

The curves for Butyl and GR-S in Figure 8 show peaks in the attenuation

as the temperature is varied. Two significant facts are obvious from the curves. The attenuation peaks become higher and are shifted to higher temperatures at higher frequencies. This phenomenon is analogous to the situation encountered in the study of losses in dielectrics. The peaks of Butyl are much broader than those of GR-S, and occur at temperatures about 40° C higher than those of GR-S. Measurements of the transmission of bulk waves from 40 kc to 10 Mc, made on the same materials, showed a similar behavior[4]. At the high frequencies, however, the attenuations were one or two orders of magnitude greater.

Figures 9 and 10 show attenuation in db per wave length as a function of frequency for different temperatures. The curve for GR-S at 5.5° C appears to peak in the frequency range measured. A comparison with the modulus *vs.* frequency curve, Figure 5, at the same temperature indicates that this peak

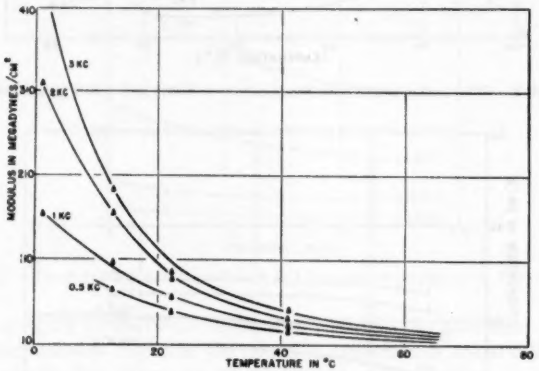

FIG. 6.—The variation of the dynamic Young's modulus with temperature for Butyl gum.

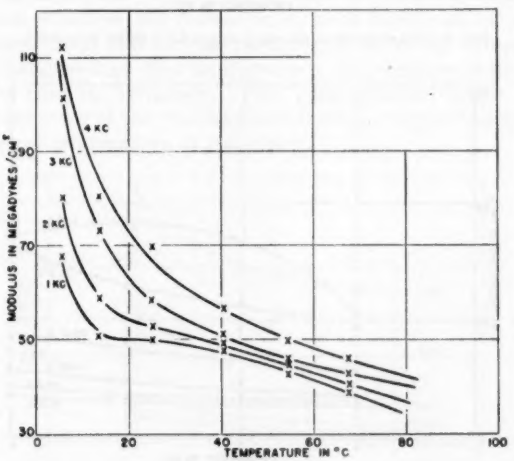

FIG. 7.—The variation of the dynamic Young's modulus with temperature for GR-S gum.

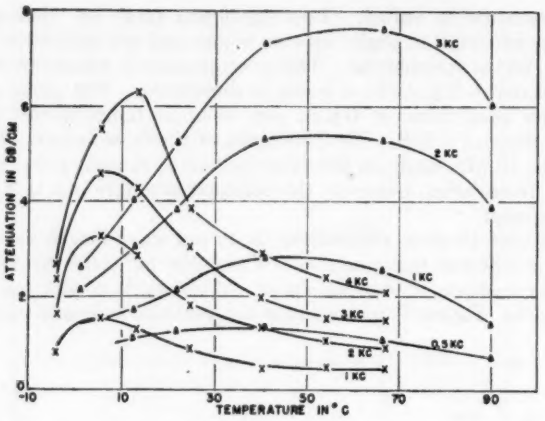

FIG. 8.—Attenuation peaks with temperature in Butyl and GR-S gum stocks.

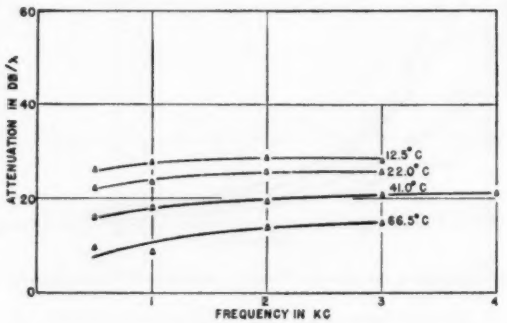

FIG. 9.—Attenuation in db/wave-length for a Butyl gum stock.

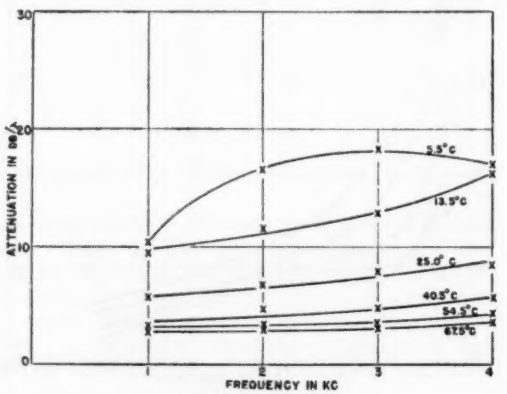

FIG. 10.—Attenuation in db/wave-length for a GR-S gum stock.

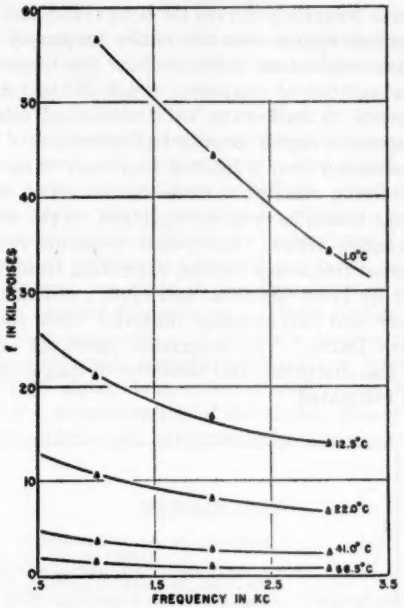

FIG. 11.—The normal viscosity coefficient as a function of frequency for Butyl gum.

corresponds roughly to the broad dispersion region in the modulus. The curves at higher temperatures indicate the possible existence of attenuation peaks at frequencies above the range of measurement. In Figures 11 and 12, the viscosity coefficient f is plotted as a function of frequency for Butyl and GR-S at different temperatures. The value of this coefficient decreases with frequency at all temperatures, but does so much more rapidly at low temperatures.

It is apparent from the curves, particularly those for attenuation *versus* frequency and temperature, that an increase in temperature produces the same effect as a decrease in frequency. This generalization might be useful in predicting the behavior of the viscosity and modulus beyond the experimentally accessible range of temperature or frequency.

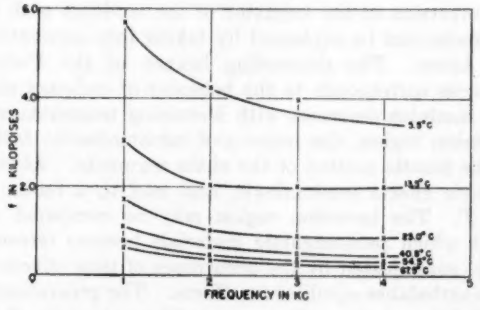

FIG. 12.—The normal viscosity coefficient as a function of frequency for GR-S gum.

The modulus *versus* frequency curves for both GR-S and Butyl indicate the existence of a dispersion region over the entire frequency range of measurement. The relaxation mechanism responsible for this dispersion would involve the assumption of a number of relaxation times of the order of 10^{-3} second. However, measurements of bulk-wave transmission at ultrasonic frequencies indicate that the dispersion region extends to frequencies of the order of 10 Mc or higher[4]. The dispersion over a limited frequency range can be attributed to a mechanism involving relaxation times of the order of $1/\omega$, whereas the entire dispersion range would have to be explained on the assumption of a wide distribution of relaxation times. Composite modulus *versus* frequency and internal viscosity *versus* frequency curves, extending from 1.5 c.p.s. to 10 Mc, are given in a paper by Ivey, Mrowca, and Guth[4], utilizing the data obtained in the present paper and unpublished material from the Polymer Physics Laboratory at Notre Dame. The relaxation spectrum resulting from these composite curves is also discussed, and the order of magnitude of the activation energies involved is estimated.

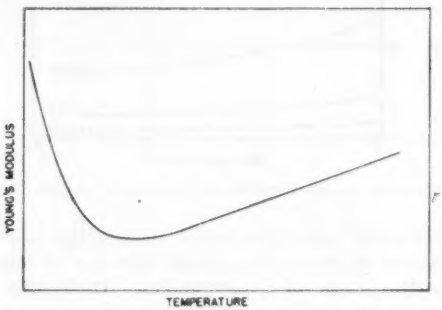

FIG. 13.—Schematic diagram showing the inversion of the dynamic Young's modulus with temperature at very low frequencies.

At frequencies below 500 cycles, as the static case is approached, the modulus-temperature curves become U-shaped as indicated in the schematic Figure 13. In the modulus-temperature curves of Figures 6 and 7, only the descending branch of the U-shaped curve is observed. The minima in such curves become sharper and shift to lower temperatures as the frequency decreases[5]. The inversion in the behavior of the modulus with temperature at very low frequencies can be explained by taking into account both inter- and intramolecular forces. The descending branch of the U-shaped modulus-temperature curves corresponds to the behavior of ordinary elastic materials, whose Young's modulus decreases with increasing temperature. For rubbers below the inversion region, the inter- and intramolecular forces overshadow the effects of the kinetic motion of the chain segments. Above the inversion region, the kinetic effects predominate, and lead to a linear increase of the modulus with T. The inversion region may be compared with the Curie temperature, at which paramagnetic materials become ferromagnetic. This simple picture is complicated by the occurrence of time effects which for some polymers may overbalance equilibrium effects. The generalized kinetic theory can be discussed by analogy to the theory of ferromagnetism[6].

SUMMARY

Velocity and attenuation measurements were made in thin strips of rubber from 0.5 to 5 kc and from −5° to 90° C to obtain the dynamic viscoelastic constants of Butyl and GR-S gum stocks. Above room temperature velocity and attenuation are higher in Butyl gum than in GR-S. In all cases, the velocity increases with decreasing temperature and increasing frequency. The attenuation shows a peak with temperature. For Butyl, the peaks are broad and occur at higher temperatures than for GR-S. For both stocks an increase in frequency gives peaks which are higher, sharper, and shifted to higher temperatures. In some instances, there are indications of peaks in the attenuation *versus* frequency at frequencies beyond our range of measurement. The behavior of the dynamic modulus in the temperature and frequency range studied is similar to that of the velocity. These results, combined with low temperature static measurements and very low frequency dynamic measurements, indicate a U-shaped modulus-temperature curve whose minimum broadens and shifts to higher temperatures with increasing frequency. This may be explained by a generalization of the kinetic theory of rubber elasticity, taking into account intra- and intermolecular forces, and considering time effects.

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PROPAGATION OF ULTRASONIC BULK WAVES IN HIGH POLYMERS *

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INTRODUCTION

The viscoelastic constants of rubber at audiofrequencies have been obtained by measurement of traveling or standing waves in strips of the material[1]. There are intrinsic difficulties in the extension of these methods to higher frequencies, since, in order that the problem remain one-dimensional, the wave length must be long in relation to the cross-section of the sample used. This would involve the use of impossibly thin strips at high frequencies. At ultrasonic frequencies, measurements of bulk-wave transmission can be more readily carried out.

Bulk-wave properties in glasses have been studied at these frequencies by optical methods[2]. Opaque solids such as metals have been studied by passing a continuous wave train through plane sheets of the material immersed in a liquid[3]. Interference patterns result due to reflections at the interfaces. From a study of the change in these patterns, when the sample thickness is changed by rotation, the elastic constants can be deduced. A more convenient technique is to use a pulsed ultrasonic beam so that a directly transmitted signal can be observed without the complication of interference. This method has been used extensively for organic[4] and for polymeric[5] liquids. Measurements of rubber, using this pulse technique, have been made in various polymers at fixed frequencies of 10 and 30 Mc per second by Nolle and Mowry[6]. Sack and Aldrich[7] have recently carried out measurements of hysteresis losses in elastomers in the range 0.5 to 6 Mc per second, using frequency-modulated waves to avoid standing wave effects. In the present work, a pulsed ultrasonic wave was used to investigate the viscoelastic constants of three types of rubbers in the frequency range from 40 kc per second to 10 Mc per second, and the temperature range from $-60°$ to $60°$ C.

EXPERIMENTAL METHOD

A pulsed compressional wave is generated and received in a liquid by a pair of crystal transducers. By observing the time shift and change in amplitude of the received signal when a rubber sample is inserted in the path of the beam, the bulk-wave velocity and attenuation can be calculated. The duration of the pulse is such that interference effects do not occur in the first signal received. However, the pulses used are of sufficient length for the group velocity of the pulse to be assumed equal to the phase velocity of continuous waves of the same frequency.

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A schematic diagram of the apparatus is shown in Figure 1. The synchroscope triggers the pulse generator at the same instant that it starts its sweep. A negative pulse from the pulse generator cuts off a tube which normally short circuits the tank of the oscillator. Thus the oscillator is opened for the duration of the pulse. The oscillations are amplified and fed to the transmitting crystal, which generates an interrupted train of waves in the transmitting liquid. The crystals used are of sufficient cross-section to assure a well collimated plane wave. This wave is picked up by the receiving crystal, and the resulting signal is amplified and fed into the peak reading voltmeter and the synchroscope. When a rubber sample is inserted in the path of the beam, the wave pattern on the synchroscope screen shifts in position and changes in amplitude. Since a part of the liquid path has been replaced by the sample, the velocity and attenuation in the sample relative to the transmitting liquid can be obtained.

The transmitting liquids used had negligible attenuation compared to that of the rubber, so that the sample attenuation was obtained directly, assuming

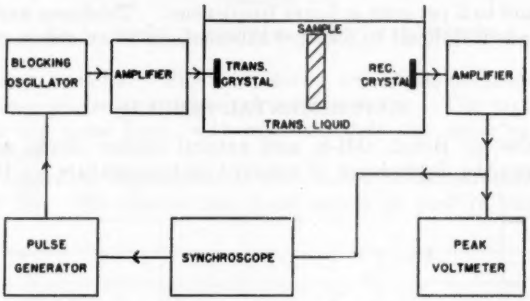

FIG. 1.—Schematic diagram of apparatus for measuring bulk-wave propagation constants.

no reflection at the liquid-sample interfaces. This assumption is valid if liquids of approximately the same acoustic impedance as rubber are used. The discrepancies due to reflections were studied by using samples of varying thickness, and observing the attenuation due to differences in thickness. This also guarded against interpreting pseudoattenuations due to standing waves as true attenuations when it was necessary to use very thin samples. It was found that the attenuation at these frequencies is so large that both of these effects may be neglected.

The velocity in the sample was obtained from the relationship:

$$C = DC_L/(D \pm C_L\Delta t)$$

where D = sample thickness (measured by a dial micrometer at each temperature), C_L = velocity in the liquid, and $\pm\Delta t$ is the time shift observed on insertion of the sample; C_L was measured by an interferometer method. The relative distance between the crystals could be changed by a calibrated screw drive, and the resultant fringe shift observed on the synchroscope. The velocity in the transmitting liquid was measured at each temperature to an accuracy of 0.5 per cent or better. Any desired precision could be obtained in this measurement. The overall accuracy of the method was ascertained by measuring the velocity of transmission through several liquids enclosed in a

thin-walled cell. Measured values for the velocity in several liquids checked with those reported in the literature to better than 0.2 per cent.

Measurements were made in the temperature range $-60°$ to 60° C. Above 0° C water was used as a transmitting liquid because of its negligible attenuation and desirable acoustic impedance. Below 0° C an ethylene glycol-water mixture was used, which had negligible attenuation down to about $-30°$ C. Below this temperature a small correction had to be made. The velocity in this mixture is higher than it is in water, which is advantageous because the velocity in rubber is higher at lower temperatures. Thus, the mismatch at the interfaces is minimized and can be neglected. Another advantage is that the error in velocity measurements is a minimum when $C = C_L$, since errors in D and Δt are then eliminated.

x-Cut Rochelle salt crystals were used in the frequency range of 40 kc to 1 Mc and x-cut quartz crystals at frequencies from 1 Mc to 10 Mc. Measurements were made at 44 kc, 400 kc, 1 Mc, 3 Mc, and 10 Mc. At each frequency, complete velocity-temperature and attenuation-temperature curves were obtained. Velocity measurements were accurate to within 2 per cent at high frequencies and to 5 per cent at lower frequencies. Thickness and composition variations made it difficult to measure attenuations to an accuracy better than 10 per cent.

EXPERIMENTAL RESULTS

The results for Butyl, GR-S, and natural rubber stocks are presented. Figure 2 shows the dependence of velocity on temperature for the three gum

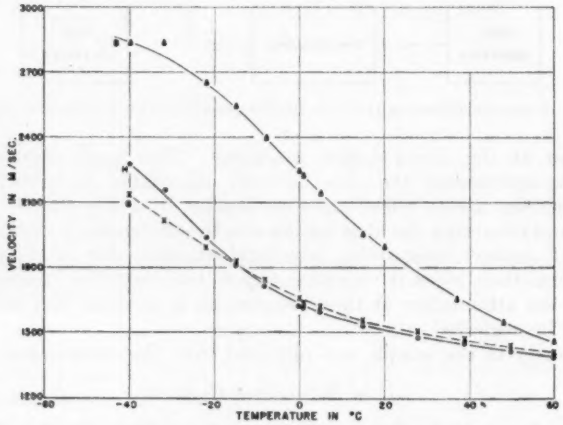

FIG. 2.—Bulk-wave velocity vs. temperature at 1 Mc per second for Hevea, GR-S, and Butyl rubbers (designated by H, G, and B).

stocks at a frequency of 1 Mc. The velocity increases with decreasing temperature, the Butyl showing the most marked change. Natural rubber and GR-S are indistinguishable above 0° C. There is some indication that the curves level off at both high and low temperatures. The general behavior is the same at all frequencies. This is shown in Figure 3, where velocity-temperature curves are plotted for Butyl at all frequencies. An increase in velocity

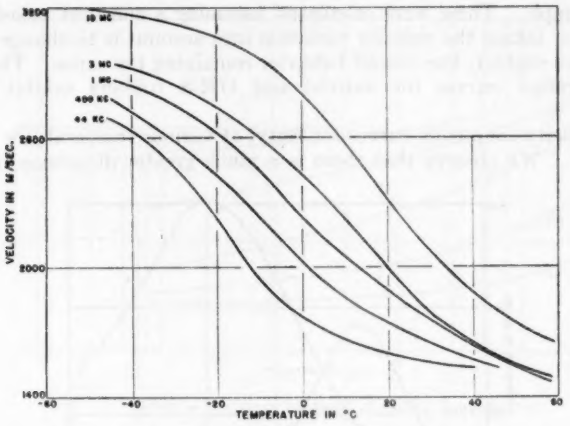

FIG. 3.—Velocity *vs.* temperature for Butyl at all frequencies.

with frequency is noted. Figure 4 shows velocity-temperature curves for GR-S at all frequencies, showing much less dispersion. The curves for natural rubber have the same form, with approximately the same values as those shown for GR-S.

Figure 5 shows the dependence of attenuation on temperature for the three stocks at 10 Mc. We observe that these curves all peak in this temperature

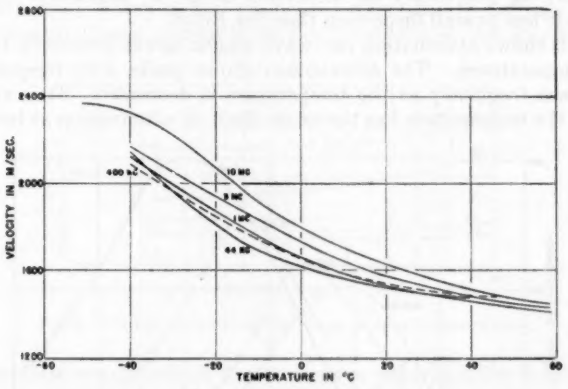

FIG. 4.—Velocity *vs.* temperature for GR-S at all frequencies.

region. Similar behavior has been observed by Nolle and Mowry[6] for some synthetic rubbers and by Mason[8] for other polymers. These curves have relatively the same form at all frequencies, but as the frequency is decreased the curves decrease in amplitude and shift to lower temperatures, as indicated by Figure 6, which shows attenuation-temperature curves for Butyl at all frequencies. The attenuation per unit length of sample decreases very rapidly with decreasing frequency. The attenuations per wave length are plotted on

the same graph. These were calculated assuming a constant velocity, as the only effect of taking the velocity variation into account is to change the shape of the curves slightly, the overall behavior remaining the same. The attenuation-temperature curves for natural and GR-S rubbers exhibit a similar behavior.

The velocity-frequency curves for Butyl at various temperatures are shown in Figure 7. We observe that there is a much greater dispersion in the 0° C

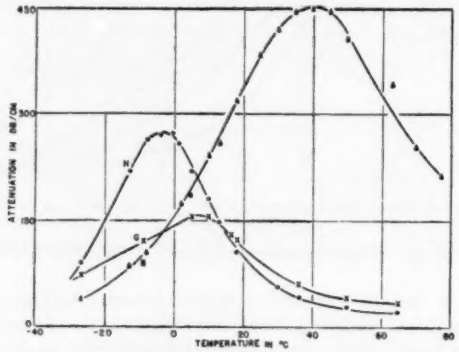

FIG. 5.—Bulk-wave attenuation *vs.* temperature at 10 Mc per second for Hevea, GR-S, and Butyl rubbers.

region than at ±40° C. Figure 8 shows velocity-frequency curves for natural rubber, showing practically no dispersion at 40° C, maximum dispersion at −20° C, but less overall dispersion than for Butyl.

Figure 9 shows attenuation per wave length *versus* frequency for Butyl at various temperatures. The attenuation shows peaks with frequency, which shift to lower frequency as the temperature is decreased. It is evident that decreasing the temperature has the same effect on attenuation as increasing the

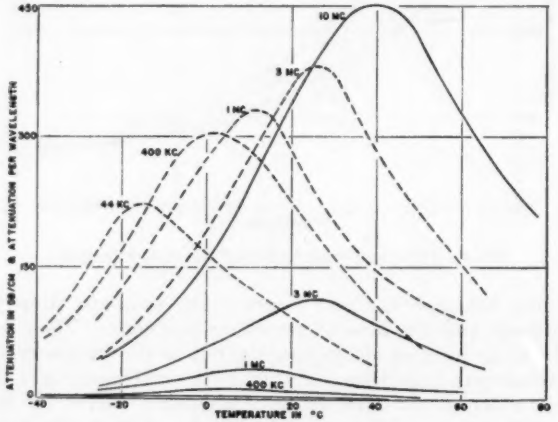

FIG. 6.—Attenuation per cm. (solid curves); and attenuation per wave length (dashed curves, arbitrary scale) for Butyl at all frequencies.

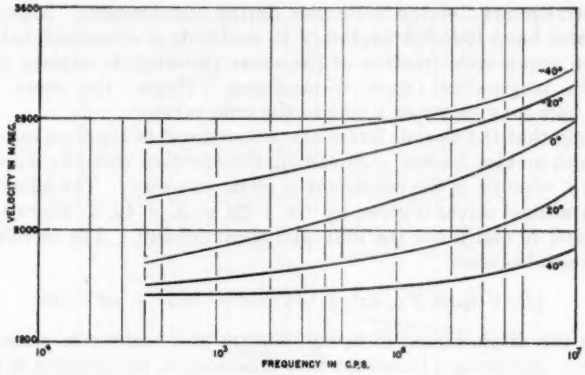

FIG. 7.—Velocity *vs.* frequency for Butyl at various temperatures.

frequency, *i.e.*, a given change in attenuation can be produced by either an increase in frequency or a decrease in temperature.

THEORY

In general, four viscoelastic constants are necessary to characterize a viscoelastic material, since there are shear and compressional viscosities in addition to the shear and bulk moduli. To determine these constants then, we need not only measurements on bulk-wave transmission, but also the propagation constants for shear waves in the material. Experiments are now being performed to measure these constants at the lower end of the above frequency

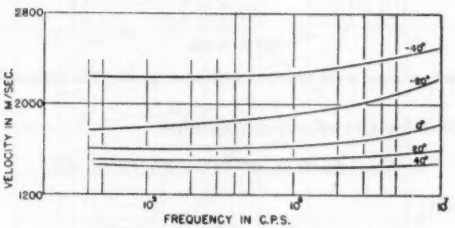

FIG. 8.—Velocity *vs.* frequency for Hevea at various temperatures.

range to correlate quantitatively the bulk wave data with the lower frequency strip data. As can be seen by comparing the present paper with the low frequency work[9], the results are qualitatively in agreement, but an exact comparison cannot be made unless the elastic constants themselves can be determined.

In the absence of shear wave data, an approximate three constant theory can be obtained by making Stokes' assumption that there is no viscosity associated with a hydrostatic compression. Recent measurements of viscous losses in ordinary and in polymeric liquids indicate that this assumption is probably not valid for such materials. For instance, Hall[10] has shown that the observed losses in water can be explained by assuming that there is a lag

in the rearrangement of the molecules during compression. Mason and coworkers[11] also have found it necessary to postulate a compressional viscosity, which is an appreciable fraction of the shear viscosity, to explain losses associated with longitudinal wave transmission. Hence, the shear viscosities computed here may be upper limits to the true values.

Assuming that the viscous forces are proportional to the time rate of change of strain, and making Stokes' assumption, the effective viscosity may be shown to be[12] $4\gamma/3$, where γ is the coefficient of shear viscosity. The effective modulus for dilatational waves is given by [13] $\lambda + 2\mu = K + 4\mu/3$, where λ is Lame's constant, and K and μ are the bulk and shear moduli. The one-dimensional wave equation becomes:

$$(K + 4\mu/3)\partial^2 u/\partial x^2 + (4\gamma/3)\partial^3 u/\partial t \partial x^2 = \rho \partial^2 u/\partial t^2$$

where u is the displacement from equilibrium of a transverse plane, and ρ is the density. Assuming a harmonic time dependence, the solution of the ampli-

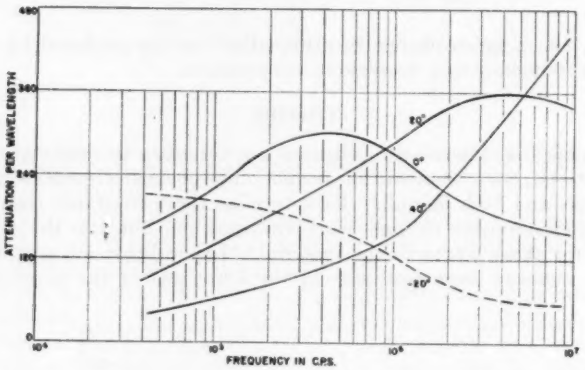

FIG. 9.—Attenuation per wave length *vs.* frequency for Butyl at various temperatures.

tube equation gives for the effective modulus:

$$K + 4\mu/3 = \rho C^2(1 - r^2)/(1 + r^2)^2$$

and for the viscosity:

$$4\gamma\omega/3 = \rho C^2 2r/(1 + r^2)^2$$

where ω = angular frequency, and the parameter $r = \alpha C/\omega = LC/8.7\omega = L\lambda/54.6$, where α = attenuation in nepers/cm, L = attenuation in db per cm., C = wave velocity in sample, λ = wave-length in sample. Hence, r is the ratio of $L\lambda$, the attenuation in db per wave length, to 54.6, the attenuation of a perfectly viscous medium.

In practice, r is usually less than 0.1, so $k + 4\mu/3$ is approximately equal to ρC^2 and $\gamma \sim LC^3/\omega^2$. Figures 10 and 11 show these quantities plotted as a function of frequency for Butyl and natural rubber at three temperatures. The effective loss factor $(4\gamma\omega/3)/(K + 4\mu/3)$ is also plotted in Figures 10 and 11, and is observed to peak with frequency, the peak shifting to lower frequencies at lower temperatures.

To discuss quantitatively the distribution of relaxation times for the ob-

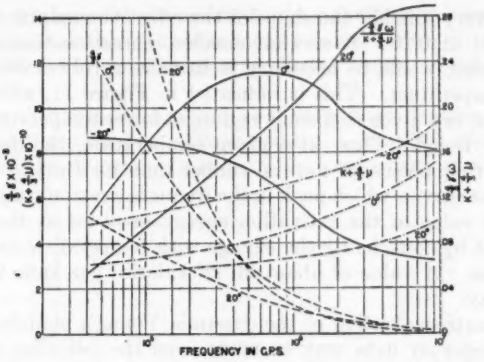

FIG. 10.—Effective modulus, viscosity, and loss factor *vs.* frequency for Butyl at 20°, 0°, and −20° C.

served dispersion, it is necessary to know K, μ, or E, Young's modulus, over the entire frequency spectrum. If, for example, μ were known from shear wave measurements, then from the data above the bulk modulus and Young's modulus could be computed, and the values for Young's modulus could be extrapolated to meet the low frequency data obtained by strip methods[9]. However, in the absence of these measurements, the following observations can be made. In general, the relaxation spectrum needed to explain the observed modulus and internal friction is broad in the audiofrequency range,

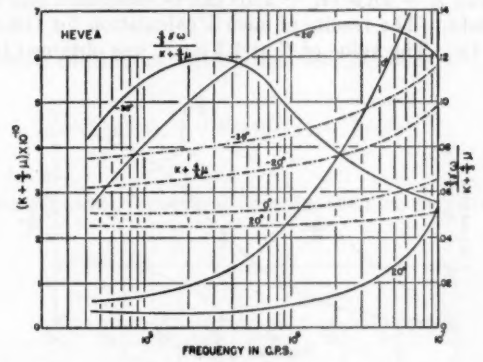

FIG. 11.—Effective modulus and loss factor *vs.* frequency for natural rubber at 20°, 0°, −20°, and −30° C.

but is sufficiently narrow in the megacycle region to be explained by assuming a few relaxation times. The relaxation mechanisms responsible for dispersion in the frequency region of this work have relaxation times of the order 10^{-6} to 10^{-8} second. The relaxation spectrum, although narrower than in the audio region, is still too broad to be explained by one relaxation time. However, any small portion of the curves could be represented by one or two relaxation times, as has been noted also by Sack and Aldrich[7]. For example, two relaxation times of approximately 5×10^{-6} second and 4×10^{-8} second could be

used to explain very roughly the shape of the effective modulus and loss factor curves for Butyl at 0° C. Somewhat smaller relaxation times, of the order 10^{-7} to 10^{-9} second, would be necessary to fit natural rubber and GR-S curves at the same temperature. This is indicated in Figure 11, which shows that dispersion occurs, in a given frequency region, at lower temperatures for natural rubber than for Butyl. Thus, at a given temperature, the dispersion would occur at higher frequencies for natural rubber than for Butyl. For the Butyl rubber loss factor curves, which peak in the frequency region studied (Figure 10) an approximate value of the activation energy involved at these frequencies may be obtained by considering the change with temperature of the frequency of maximum loss. A value of about 20 kilocalories per mole is obtained for Butyl in this way.

An approximate evaluation of the dynamic Young's modulus for comparison with low-frequency data may be made from the following considerations. Mason and coworkers[14] have shown that the high frequency dispersion in polymeric liquids appears to be due to the appearance of "crystalline" shear elasticity. Nolle and Mowry[6] have assumed that this is also true for rubber, taking the bulk modulus K as equal to that of water. This assumption appears valid in the present work, since the effective modulus curve for natural rubber at 20° C, Figure 11, appears to level off below 100 kc, approaching as a limit the value 2.25×10^{10} dynes per sq. cm., which is the bulk modulus of water[15]. It is reasonable to assume then that, at low frequencies, just as in the static case, μ is negligible in comparison[16] with K. Taking K equal to the limiting value of $K + 4\mu/3$ at the low frequencies, and assuming it is constant, μ can then be calculated at the high frequencies from the observed change in $K + 4\mu/3$. Thus, $E = 3K\mu/(K + \mu/3)$ can be computed and compared with low-frequency data. The results of such a calculation for GR-S at 20° C are given in Figure 12. The value of E at 1.5 c.p.s. was obtained from free vibra-

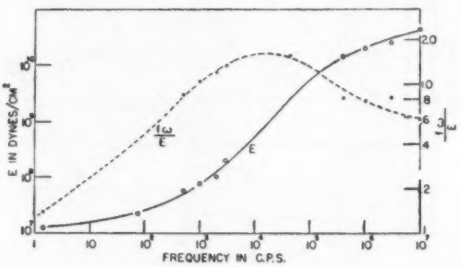

FIG. 12.—Young's modulus and loss factor vs. frequency for GR-S at 20° C, showing correlation with low-frequency data.

tion data[17], those at 30 and 212 c.p.s. from resonance techniques[18], and those from 1 to 4 kc from strip method data[9]. Shown also in Figure 12 is the loss factor $f\omega/E$, where f is the "Young's modulus" viscosity[9], also obtained at low frequencies from the above sources. Figure 13 shows E and $f\omega/E$ for Butyl rubber at 20° C, calculated under the same assumptions. Since the effective modulus curves for Butyl, Figure 10, do not completely flatten out at low frequencies, the value of K must be approximated, and the calculations

are therefore less accurate. For both Butyl and GR-S the loss factor exhibits peaks, and these peaks occur approximately in the region of maximum change in modulus. The dispersion region of Butyl occurs at slightly lower frequencies than that of GR-S.

We observe that dispersion occurs over at least six decades of frequency for both GR-S and Butyl rubber. Consequently, a complete spectrum of relaxation times would be necessary to explain the mechanisms involved. For such

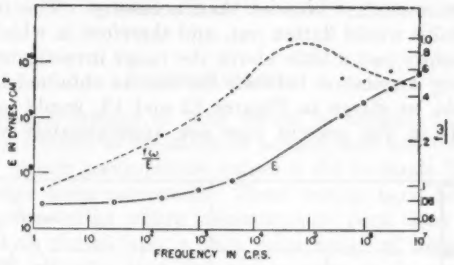

FIG. 13.—Young's modulus and loss factor *vs.* frequency for Butyl at 20° C, showing correlation with low-frequency data.

a relaxation phenomenon:

$$E(\omega) = \sum_{j=0}^{\infty} A_j/(1 + 1/\omega^2\tau^2)$$

and if we assume a continuous distribution, this becomes:

$$E(\omega) = \int_0^{\infty} F(\tau)d\tau/(1 + 1/\omega^2\tau^2)$$

If the dispersion extends over several decades, then we may treat a given term

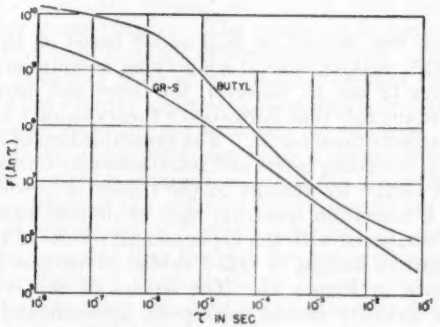

FIG. 14.—Approximate strength of the relaxation spectrum *vs.* relaxation time for GR-S and Butyl at 20° C.

in the series as a step function[19], and write:

$$E(\omega) \cong \int_{1/\omega}^{\infty} F(\tau) d\tau$$

The quantity $F(\tau)$ may be called the strength of the relaxation spectrum. Figure 14 shows $F(\ln \tau)$, which is the strength of the relaxation spectrum between $\ln \tau$ and $\ln \tau + d \ln \tau$, plotted as a function of τ, for GR-S and Butyl at 20° C, using E from Figures 12 and 13. The approximations lead to a distribution which is somewhat broader than necessary. The frequency region in which the modulus would flatten out, and therefore in which $F(\ln \tau)$ would decrease, is apparently just a little above the range investigated.

The satisfactory correlation between the results obtained by low and high frequency methods, as shown in Figures 12 and 13, would indicate that the assumptions made in the present case are approximately valid. A broad

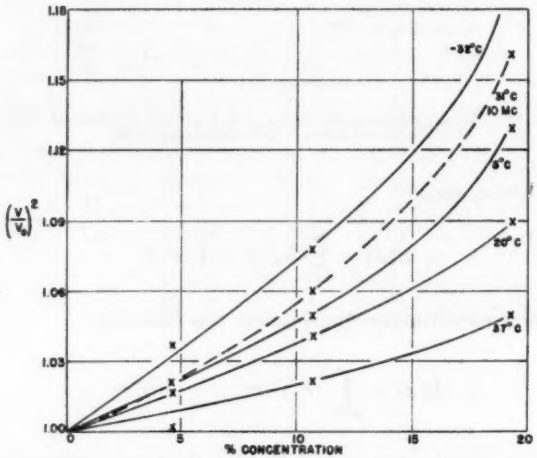

FIG. 15.—Relative modulus *vs.* volume concentration of carbon-loaded GR-S at 1 Mc and 10 Mc (dashed curve).

relaxation spectrum was derived by Kirkwood[20] based on the network model of James and Guth[21], making several simplifying assumptions. For the data embodied in Figures 12 and 13, however, the inter- and intramolecular forces play such an important role that Kirkwood's theory cannot be applied quantitatively, since it neglects these forces. The generalization of the kinetic theory of rubber elasticity, including inter- and intramolecular forces, is being carried out by James and Guth[22] by analogy to the theory of ferromagnetism. It is to be hoped that a relaxation spectrum may be derived based on this generalized theory and compared with the experimental results of the present paper.

The effect of carbon loading in GR-S rubber at various temperatures and frequencies is shown in Figure 15. The square of the relative velocity is plotted, since this quantity should correspond approximately to the relative modulus. At 1 Mc, the increase in modulus with loading is much greater at lower temperatures. The same effect is achieved by going to higher fre-

quencies, as can be seen from the 10-Mc curve. The curves approach, at low temperature or high frequency, the theoretical curve derived by Guth[28]:

$$E/E_0 = 1 + 2.5c + 14.1c^2$$

where E/E_0 is the relative static modulus and c is the concentration.

The effect of cure was also investigated, and found to be negligible. However, the undercured and overcured samples used probably did not differ greatly in the amount of cross-linking from the optimum-cured samples used. Consequently, little can be said about the effect of cross-linking and polymerization.

CONCLUSIONS

The propagation constants of bulk waves in natural, GR-S, and Butyl rubbers have been studied as functions of temperature and frequency. From these data, under certain assumptions, values of the dynamic Young's modulus and loss factor have been computed. These results have been extrapolated to the low frequency region where measurements have been made by other methods, and curves drawn over a very wide range of frequency. The resulting correlation indicates that the assumptions made are approximately correct. However, these calculations are only tentative and are dependent for corroboration on measurements of shear wave propagation in the high frequency region. Such measurements are at present being attempted. It is to be hoped that an accurate knowledge of viscoelastic behavior over the entire frequency spectrum will allow a quantitative discussion of the relaxation mechanisms and activation energies involved. From this, a better picture of molecular behavior might be obtained.

SUMMARY

The propagation of supersonic waves in bulk rubbers has been studied from 40 kc per second to 10 Mc per second and from $-60°$ to $60°$ C. The wave velocity was found to increase with decreasing temperature, level off both at high and low temperatures, and increase slightly with frequency. Peaks in attenuation as a function of either temperature of frequency were observed; these occurred at lower temperatures for lower frequencies. The peaks of Butyl, a high-loss rubber, are broader and higher than those of GR-S and Hevea, which are lower-loss rubbers. The results are in qualitative agreement with data obtained by strip methods at audiofrequencies. However, for bulk waves the real and imaginary parts of two elastic constants, the bulk and shear moduli, determine wave velocity and attenuation; hence, independent measurements of shear wave properties are necessary to evaluate these constants. A three constant theory is discussed, assuming a shear viscosity only, so an effective modulus $K + 4\mu/3$ is obtained, where K and μ are the bulk and shear moduli. Relaxation times of the order 10^{-6}–10^{-8} second are indicated. Approximate values of the dynamic Young's modulus are obtained from the effective modulus by assuming that the high frequency dispersion is due to the appearance of a "crystalline" shear elasticity. These results are correlated with low frequency data, and the dynamic Young's modulus and the loss factor are plotted. The loss factor exhibits a maximum in the dispersion region. Results are plotted in the range from 1 to 10^7 c.p.s., which covers a

wider range of frequency than earlier investigations. The necessary distribution of relaxation times is discussed.

APPENDIX

Compositions and Cures of Stocks Used

Hevea gum

Crepe or smoked sheet	100
Zinc oxide	3
D.P.G.	1
Sulfur	5

Cured 30 minutes at 50 lb. steam (147° C)

Butyl gum

Butyl	100
Zinc oxide	5
Tuads	1
Sulfur	1

Cured 60 minutes at 147° C

GR-S gum

GR-S	100
BLE	1
BRT No. 7	5
Zinc oxide	5
Santocure	1.2
Stearic acid	2.5
Sulfur	1.7

Cured 70 minutes at 141° C

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[15] This value is calculated from the observed bulk-wave velocity of 1.5×10^5 cm. per second in water at 20° C.

[16] This is equivalent to assuming that, at low frequencies, Poisson's ratio approaches a value of one-half, which is known to be true of rubber.

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MASTICATION OF RUBBER. I*

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In this paper a short record is given of some experiments on the mastication of rubber and on the influence of mastication on the properties of vulcanized rubber. The matter has been examined from a technical standpoint; the purely chemical aspects[1] have been left more or less aside.

It was our purpose to carry out measurements on the influence on plasticity of time and temperature of mastication and mixing, of the power used, of the influence of several fillers and softeners, and of sulfur, accelerators, and some other chemicals commonly admixed into rubber. Besides, the authors wanted to make mechanical tests, combined with aging, on vulcanized stocks, plasticized in different ways. The work was carried out several years ago, and part of it has lost interest because more elaborate studies have since been published. These parts are, therefore, omitted or mentioned in a few words. In this paper our experiments are related under two separate headings:

A. Influences in unvulcanized stock.

B. Influences in vulcanized stock.

INFLUENCES IN UNVULCANIZED STOCK

The measurement of plasticity[2] was carried out by compression between parallel plates by the Williams' method[3], using sometimes Hoekstra's balance plastometer[4], in other cases his steam plastometer[5].

The plasticity measured by means of the first instrument is expressed as thickness in mm. after compression for 10 minutes at 70° C with a force of 5 kilograms and a surface of the upper (smaller) die of 1 sq. cm. (*D* 10); the second instrument gives *D* 1/4: compression after 15 seconds at 100° C with a force of 10 kilograms and with the same surface of the die.

As has been shown in another paper[5], both values D 10 and D 1/4 give in the first instance a measure of the same rheologic properties of rubber; they can be interchanged by the use of a chart already published[6].

The plasticity-time curve on laboratory rolls was found to be reproducible if all items which influence the process, like weight and quality of rubber, position of rolls (nip), way of cutting rubber on the rolls, temperature of rubber, time of mastication, etc., are kept constant. If these factors are not kept rigorously constant, as was the case in a number of preliminary runs, wide variations in plasticity were found after equal periods of mastication; for instance, variations from 0.07–0.31 after 60 minutes' masticating at normal

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol, 25, No. 1, pages 43–55, June 1949.

temperature. However, the reproducibility is not perfect, as is shown in Table 1.

TABLE 1

MASTICATION OF THE SAME SHEET RUBBER ON DIFFERENT DAYS

Date	D 1/4 after mastication for 10 min.	20 min.	30 min.	40 min.	52 min.
Oct. 25	0.365	0.255	0.205	0.18	0.16
Nov. 4	0.37	0.265	0.22	0.20	0.18
	0.38	0.26	0.22	0.20	0.18
Nov. 7	0.315	0.22	0.18	0.15	0.14
Nov. 10	0.35	0.24	0.20	0.18	0.165
	0.355	0.24	0.20	0.18	0.17
Nov. 11	0.335	0.23	0.195	—	—
	0.365	0.24	0.195	—	—

Mastications executed on the same day are seen to be in accord. Mastications on different days show differences. It may be possible that the condition of the atmosphere has something to do with this.

As has been shown already[5], there was found to be a little hardening of raw rubber (sheet as well as crepe) during the first minutes of mastication, when the rubber runs in a loose blanket full of holes around the first roll and no bank has yet been formed. Piper and Scott[6] found the same effect with GR-S in a Banbury mixer.

This phenomenon is the more marked the lower the temperatufe of mastication, undoubtedly because real mastication begins only after a bank is formed, which takes more time at lower temperatures. Before this, the rubber is only stretched and stressed, and this causes the hardening.

4. *The influence of the temperature* in the rubber during the process of mastication is very marked. Plasticization is strongest at lower temperatures, as is well known[7].

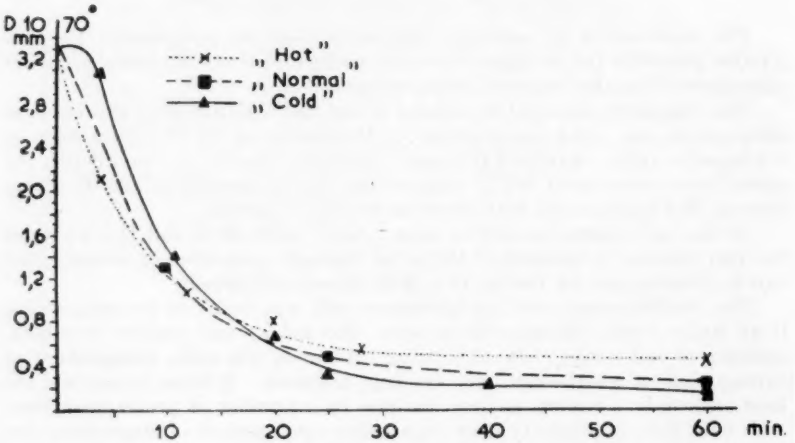

FIG. 1.—Mastication of sheet rubber on factory rolls. Average temperature in layer during mastication: hot 92° C, normal 77° C, cold 58.5° C

Figure 1 shows plasticity (D 10)-time curves for factory rolls, where mastication at different temperatures was carried out. Variation of the temperatures of these rolls was, however, limited. The temperatures given are those in the layer. By a special technique we determined the temperature of the rubber while it was running on the rolls, using a needle-shaped thermocouple. In the rubber bank between rolls, average temperatures of 134, 94 and 82° C were found on laboratory rolls.

As a conclusion to these observations it can be said, that the best way for breaking down rubber on rolls is to begin with rather hot rolls and heated rubber; as soon as the rubber is running round the rolls, these should be quickly

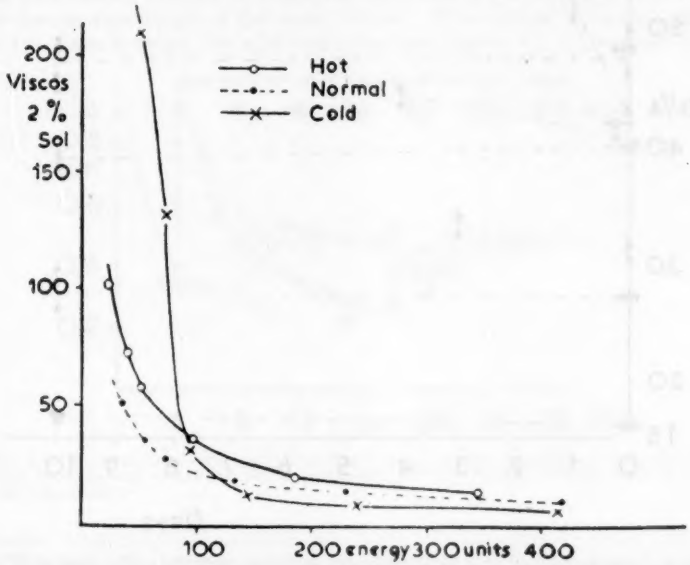

FIG. 2.—Relations between viscosities of 2 per cent solutions of rubber masticated on laboratory rolls and energy used by the masticator. Average temperature in rubber layer during mastication:
hot 79° C
normal 69° C
cold 49° C

cooled. Unfortunately, with most factory mills, quick cooling is not possible.

The energy used in the process of mastication was determined at different temperatures. Energy-viscosity curves[8] on laboratory rolls are given in Figure 2. Here the viscosities of 2 per cent rubber solutions in benzene were measured instead of plasticities, these determinations being carried out before the plasticity measurements were standardized. These viscosities run fairly parallel to the compression plasticity. The energy was computed from the readings on a wattmeter, connected to the electric motor which drove the rolls. The reason why mastication on cold rolls begins only after a considerable amount of energy has been uselessly wasted lies in the delayed formation of a bank, as mentioned.

If this retarded start in plasticization on cold rolls is disregarded, one can state that, in cold mastication, not only less time but also less energy is needed to reach a certain plasticity.

These statements confirm the conclusion drawn as to the best way of masticating rubber[8].

Storage at 70° C affects the plasticity to some extent. The investigation of plasticity changes of masticated pure sheet at 70° C was only extended over 10 days, because oxidation interfered on longer storage. During the first days at 70° C, the hardness of the rubber increases somewhat, as is shown by the following examples (see Figure 3).

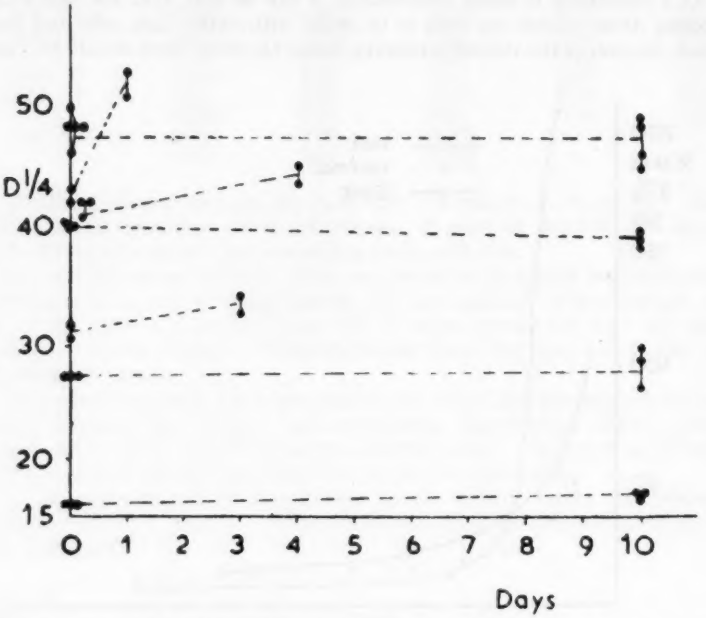

FIG. 3.—Increase and decrease in hardness of seven samples of masticated rubber stored at 70° C.

On prolonged storage at 70° C, the softness increases again, probably because of some oxidation setting in.

In general, it may be concluded that changes in softness of masticated pure rubber (sheet) on storage are of no importance during the periods which normally occur in rubber factories. Recovery does increase, however[9]. The authors made a remarkable observation during storage of thoroughly plasticized rubber at 70°: pure sheet was masticated 52 minutes at normal temperature, after which it was so soft that holes punched in the sheet slowly disappeared at 70° C; after 1 day at 70° C, however, newly-punched holes did not show flow any more. This shows without doubt that the yield value (or better: the very high viscosity at very low stresses) of masticated rubber increases markedly on storage at elevated temperatures. Differences in deformability at low shearing stresses have a greater effect on plasticity determinations made by compression between parallel plates of large extent than on those made by compression between dies of limited surface used by the authors.

The effect of fillers on the plasticity of rubber mixtures is a matter of great importance to rubber manufacturers and has, therefore, been investigated by

several authors. The problem of determining a stiffening value for a filler, that is, to determine the degree in which a certain filler influences the softness of a rubber batch in which it has been mixed, is complicated by the fact that one filler mixes much more easily into rubber than another.

For this reason the following method was chosen for determining the stiffening value[4].

Sheet rubber was masticated in our standardized way on a laboratory mill. During this mastication the plasticity-time curve was determined by means of the steam plastometer and plotted on mm. paper. After mixing the filler in, the plasticity-line was again followed for some time. The plasticity-time curve of the pure rubber was now extrapolated by means of the complete mastication curve for another batch of the same rubber. The vertical distance between these two lines is called the *stiffening value* (see Figure 4). This method was

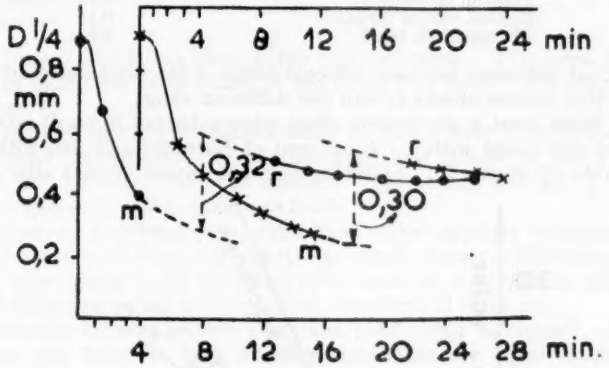

FIG. 4.—Determination of stiffening value of 20 per cent by volume of gas black in masticated rubber Plasticity determinations were taken during mastication and after mixing. Mixing began at point *m* and was ready at point *r*.

controlled by mixing several fillers into rubber in two different ways, first after as little mastication of the sheet as possible and, secondly, after the rubber had been thoroughly masticated.

The results are shown in Figure 4 and in Table 2. As is seen from the figure, the plasticity reached with each filler after the same total time on the rolls is the same, independent of the moment at which the mixing began. Indeed, it was found with most mixes that the mastication proper proceeds with the same velocity before, during, and after the mixing.

TABLE 2

STIFFENING EFFECT OF FILLERS, DETERMINED AFTER DIFFERENT DEGREES OF PLASTICIZATION OF THE PURE SHEET

	Mixed into rubber after mastication			
20 vol.-per cent	Minutes mastication before mixing	Stiffening value found	Minutes plastication before mixing	Stiffening value found
Micronex	4	0.32	11	0.30
Thermatomic	4	0.06	14	0.07
TiO_2	5	0.18	14	0.16
Whiting	5	0.09	12	0.8

Zinc oxide gave difficulties: this filler exerts a slow softening action after it has been mixed into the rubber.

The exactness of the method, though not very high in itself, is thought to be better than with other empirical methods.

Some stiffening values for 20 vol.-per cent of fillers were found as follows:

TABLE 3

STIFFENING VALUES OF FILLERS (20 VOL.-PER CENT)

Micronex	0.31
Titanium dioxide	0.18
Whiting (precipitated)	0.18
Zinc oxide	0.16
Dixie clay	0.16
Barium sulfate (precipitated)	0.15
Whiting (ground)	0.13
Barium sulfate (ground)	0.11
Thermatomic black	0.7

The great difference between different forms of the same chemical material indicates that surface effects govern the stiffening value.

Some fillers exert a plasticizing effect when admixed in small quantities[10]. This effect was found with 1 vol.-per cent of Micronex and also with 3 parts of zinc oxide (*cf.* Figure 5). Softening does not appear at once after the filler

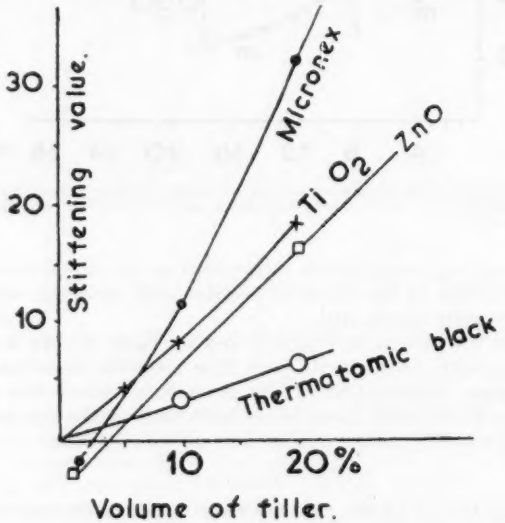

FIG. 5.—Stiffening values of Micronex, titanium dioxide, zinc oxide, and Thermatomic black in different concentrations.

has been taken up by the rubber on the rolls, but takes several minutes of mixing before the softening effect appears in the plasticity-time curves.

The stiffening effect of fillers increases approximately linearly with the percentage of fillers (see Figure 5).

On storage at room temperature, mixes of rubber and fillers generally stiffen to a certain degree. The effect is in most cases not very strong, as can

TABLE 4

PLASTICITY OF RUBBER MIXES ON STORAGE AT ROOM TEMPERATURE. MIXES WITH 20 VOLUME-PER CENT OF FILLER

	Plasticity D 1/4 direct after mixing	After storage	Days
Calcium carbonate (ground)	0.31	0.35	29
Calcium carbonate (precipitated)	0.31	0.35	29
Barium sulfate (ground)	0.29	0.265	29
Barium sulfate (precipitated)	0.38	0.355	29
Talc	0.48	0.54	33
Gas black (Micronex)	0.61	0.79	26
Gas black (Micronex)	0.50	0.64	15
Gas black (Micronex)	0.38	0.53	14
Zinc oxide	0.52	0.565	17
Zinc oxide	0.30	0.36	63
Lithopone	0.52	0.545	10

be seen from Table 4; gas black is the only exception. This remarkable slow process of hardening of mixtures of gas black and rubber was also found by Stamberger[11].

The effect of softeners on the plasticity of pure rubber is remarkably small. It was found that paraffin oil, lubricating oil, and spindle oil had a softening value of 0.01 for every per cent admixed. For stearic acid and a plasticizer like Plastogen double this value was found.

If, however, a softener was given to a rubber mixture containing a considerable amount of filler, the effect was much greater. This means that a softener only comes to its full effect when used in combination with a filler. A list of softening values of softeners is, therefore, of little use.

Accelerators have in general a marked plasticizing influence[12]. Diphenylguanidine was found to have an effect approximately equal to stearic acid. Accelerene is a few times stronger.

Whereas most mixes are stiffening a little on storage (see Figure 6), a mix with 2 per cent Accelerene (*p*-nitrosodimethylaniline) went down from 0.18 to 0.09 in 9 days and began to flow at room temperature.

Sulfur acts also to a slight degree as a softener, but seems to retard the plasticizing action on the rolls, while it induces a little stiffening of the batch

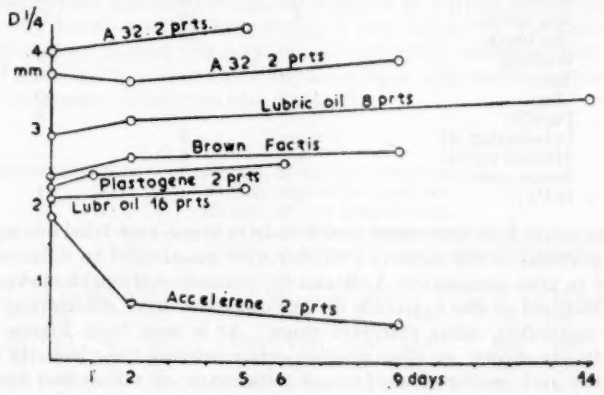

FIG. 6.—Plasticity changes of rubber-softener mixtures on storage.

on storage. These latter effects can both be ascribed to a slight vulcanization or prevulcanization. The effect is greater in mixes with accelerator[13].

The retarding action was stated by mixing 10 parts of sulfur in 100 parts of rubber. If the sulfur was mixed in after 4 minutes' mastication, the plasticity after 26 minutes on the rolls was 0.25; if the sulfur was mixed in after 12 minutes, the ultimate plasticity after 26 minutes was 0.21. Yet, the sulfur in itself had a softening action of 0.02 and the same rubber, milled for 26 minutes, showed 0.19 plasticity.

TABLE 5

PLASTICITY D 1/4 OF MIXES WITH AND WITHOUT SULFUR ON STORAGE

	100 R 10 S	100 R	100 R 3 S 1 D.P.G. 5 ZnO	100 R 0 S 1 D.P.G. 5 ZnO
Immediately after mixing	0.27	0.20	0.25	0.28
1 day old	0.305	0.202	0.31	0.32
2 days old	0.305	—	—	—
6 days old	0.315	—	—	—
23 days old	—	—	0.32	0.31
Increase in per cent:				
After 1 day	13	1	24	14
After 24 days	—	—	28	11

As has been described[14], benzidine exerts a definite stiffening action. This was confirmed by us and also the optimum concentration found at ⅛ per cent. At this point the stiffening value was 0.11.

INFLUENCES IN VULCANIZED STOCK

9. *The influence of mastication of rubber and rubber mixes on its properties after vulcanization* was studied on three types of rubber mixes, which were considered as representing pure-gum A, tread B, and wire insulation C mixes:

TABLE 6

COMPOSITION OF MIXES A, B AND C (VOL.-PER CENT)

	A	B	C
Rubber	100	100	100
Sulfur	3	3, 5	5
Zinc oxide	5	10	50
Gas black	—	30	—
Whiting	—	—	50
Talc	—	—	50
Clay	—	—	50
Paraffin	—	—	4
Lubricating oil	—	2	—
Mineral rubber	—	8	—
Stearic acid	—	2	—
D.P.G.	1	1, 25	1

In these mixes first-latex sheet and first-latex crepe were tried out separately.

First, portions of the same raw rubber were masticated to different extents and mixed to give compounds A, B and C; elongation-strength curves of these mixes, vulcanized at the optimum of vulcanization, were determined with the Schopper apparatus, using standard rings. As is seen from Figure 7, where some results are shown, no close relation exists between the plasticity of masticated rubber and results of mechanical tests made on vulcanized compounds. Some correlation may exist, however, at least for mix A. Only with some

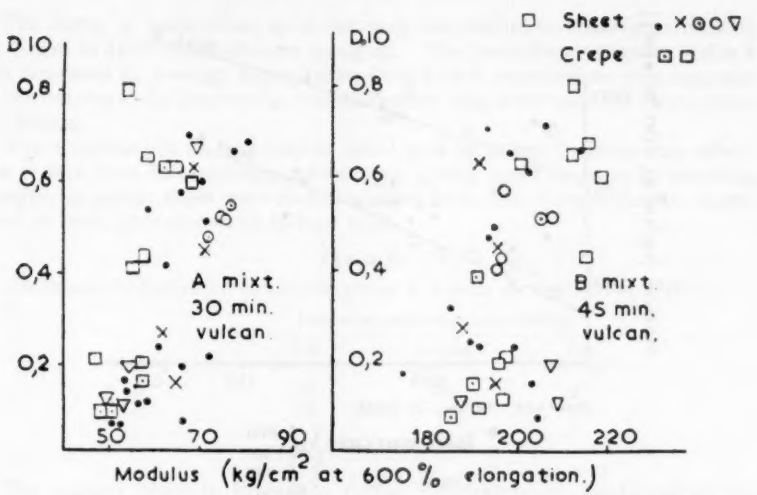

FIG. 7.—Relation between modulus of mixtures A and B and plasticity before vulcanization.

undervulcanized samples from heavily masticated rubber was the modulus found (Table 7) to be lessened. Therefore, it seems justified to say that the breaking down of molecules which takes place during the mastication of raw rubber has little effect on the network of hydrocarbon chains interlinked by sulfur bridges after mastication (vulcanized rubber). The yield value in raw rubber originates from relatively short parts of very long chains, oriented parallel and held together by forces of crystallization. The effect of this interlinking is very much decreased by a shortening of the hydrocarbon chains. On the other hand, the deformability of a cluster of hydrocarbon chains linked up by strong sulfur bonds does not change appreciably with shortening of the chains as long as every length into which the original chain has been broken up shows a number of such sulfur bonds.

An exaggerated mastication *e.g.*, 60 minutes at normal temperature, gives a 10 per cent decrease of breaking strength (see Table 7). Very short mastication (effected by putting warm rubber on cold rolls), compared with a normal process of mastication, did not give any advantage with respect to stress–strain curves of vulcanized mixes (see also Table 7).

TABLE 7

Mix A, masticated:
20 n. 20 min. at normal temperature
20 l. 20 min. at low temperature
60 l. 60 min. at low temperature
5 n. 5 min. at normal temperature
3/100° 3 min. at normal temperature after heating to 100° C

	Modulus at 600% E (kg. per sq. cm.)				Tensile strength (kg. per sq. cm.)				Elongation			
	15′	30′	45′	60′	15′	30′	45′	60′	15′	30′	45′	60′
20 n.	33	67	83	80	128	148	145	135	859	737	690	687
20 l.	33	71	85	79	114	157	150	142	822	734	694	696
60 l.	27	62	85	78	104	136	142	127	855	732	690	682
5 n.	29	71	85	82	140	180	160	175	880	758	702	692
3/100°	42	77	92	84	147	166	147	153	829	728	678	697

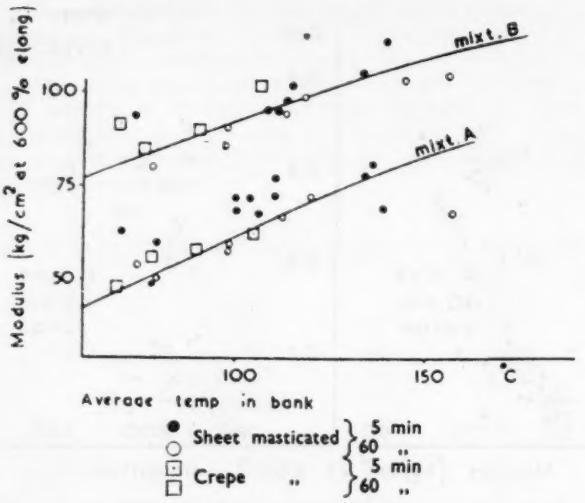

FIG. 8.—Relation between modulus and temperature during mastication. Mixture A was vulcanized 30 minutes; mixture B, 45 minutes.

The temperature of mastication.—From a great number of experiments on the influence of mastication on the mechanical properties of vulcanized rubber, Figure 8 has been constructed.

A remarkable correlation between modulus and temperature of mastication can be seen from this diagram. As there appears to be no correlation between plasticity (or viscosity) of the rubber before mastication and its modulus after vulcanization, this fact seems striking. It probably is related to the increase in nerve effected by plasticization by the effect of heat, as stated by Piper and Scott[6].

Very low temperature lessens the breaking strength. For instance, the latter fact is also evident after mastication and mixing on factory rolls.

TABLE 8

BREAKING STRENGTH AFTER VULCANIZATION OF COLD MASTICATED RUBBERS

Time of vulcanization	Mixture A (5 min.)	Masticated		Mixture B (5 min.)	Masticated	
		60 min.	Normal		60 min.	Normal
15 min.	111	108	133	124	69	148
30 min.	141	118	156	189	145	204
45 min.	147	130	146	226	181	220
60 min.	126	124	133	216	173	216

TABLE 9

DECREASE IN BREAKING STRENGTH AFTER 2 WEEKS IN GEER OVEN (70° C)

Mixture	Plasticized (before mixing)	
	5 min. (per cent)	60 min. (per cent)
A	24	27
B	42	46

The degree of mastication, in so far as it was varied in these experiments, was found to have little influence on aging. The percentages given in Table 9 each represent an average value, taken from 6 to 8 experiments with separate rubber batches. Laboratory as well as factory rolls were used for mastication and mixing.

The temperature of mastication could not be found to have any effect. This is seen from the following percentages, giving again decrease in breaking strength on aging; these were each averaged from 3 to 9 experiments, masticated on both laboratory and factory rolls.

TABLE 10

DECREASE IN BREAKING STRENGTH AFTER 2 WEEKS IN GEER OVEN (70° C)

	Method of mastication before mixing		
Mixture	Cold (per cent)	Normal (per cent)	Hot (per cent)
A	27	30	27
B	42	44	42

ACKNOWLEDGMENT

The authors desire to thank the rubber manufacturers, mentioned at the end of Part II, for permission to publish these results.

SUMMARY

Plasticity measurements with the Williams-type (parallel-plate) balance and steam plastometers confirmed the well known influence of time, temperature, and energy consumed on mastication of raw rubber on rolls. Reproducibility of results proved fairly high. The effect of storing plasticized rubber was a slow and unimportant hardening. On hot storing, hardening during the first days took place, followed by slow softening. With the steam plastometer, a stiffening value was determined for several fillers when mixed into masticated rubber. Some experiments were done on the influence of the concentration of such fillers and on the influence of softeners, accelerators and sulfur on plasticity.

The influence of the degree of mastication of the mixes on the vulcanized stocks was investigated in a few cases. Apart from the well known influence of extreme mastication on breaking strength, a remarkable influence of the temperature of mastication on modulus was found.

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MASTICATION OF RUBBER. II*

J. HOEKSTRA AND A. VAN ROSSEM

Apart from a study of the plasticity of masticated rubber and its influence on vulcanized stock as described[1], the authors studied the recovery of masticated rubber and of mixed rubber batches.

Determination of recovery can serve different purposes. From the practical point of view, recovery is of importance since it occurs after calendering or extrusion of rubber mixes, altering dimensions of formed rubber articles, and being a nuisance with respect to tolerances. As the formed goods are mostly cooled down after the deformation has taken place, part of the elastic stresses are frozen in and, on rewarming, further recovery occurs. For this reason, recovery (in the form of thermoelasticity) also occurs on free vulcanization of extruded or calendered rubber goods.

From a more theoretical point of view, the behavior of recovery on storing of rubber at different temperatures is of interest too. For recovery must be thought to be related to the occurrence of definite links (zones of local orientation resulting into a coordination of the van der Waals' forces) between the long entangled rubber molecules. These links of orientation are the cause of a sort of vulcanization (in real vulcanization their role is taken over by primary sulfur bonds). Now in storing at room temperature orientation may occur, thereby increasing the recovery. Even crystallization may set in, increasing recovery too. At higher temperatures it may be that crystallization occurs at a quicker rate; but it may be too that the crystalline spots in the rubber melt and that the orientated ones are disorientated.

Therefore it is not easy to foresee what recovery does during hot storing.

In mixing unvulcanized rubber with filler, it is possible that the particles of the filler stand in the way of the orientation and crystallization, thereby weakening the links between the long molecules. On the other hand, it is possible that some fillers replace these links by strong absorptive forces, and bring about a great increase of recovery. Apart from both these possibilities it must always be kept in mind, that particles of fillers, themselves not deformable, increase the straining of the rubber between the particles. Therefore it may be anticipated that a filled rubber behaves on compression and recovery as a much thinner sample of pure gum would do in the plasticity and recovery press: it offers more resistance to deformation and, in general, recovers to a lesser degree.

Recovery determinations were undertaken with both these views, the practical and the theoretical, in mind. Since this study was an early attempt (the experiments date from long before World War II), only provisional answers were found to the problems stated.

Method used.—At the start of the investigation recovery was measured at 70° C by exerting a certain force by means of a die till the sample was compressed from a thickness of 4 to 1 mm. Then the pressure was released, and

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 1, pages 56–66, June 1949.

readings were taken after say, 10, 20, 40, 80, etc., seconds, by means of a thickness gauge. From this recovery-time curve the recovery after 10 minutes was taken as the recovery at 70° C. The method was carried out by the balance plastometer[2]. A quicker method, which gives, however, only the end value and not the whole recovery-time line, was found by inserting an extra feeler, connected with the measuring device, in the high-speed apparatus (steam plastometer) developed by one of the authors[3] at the Rubber Institute T.N.O. (former Netherlands Government Rubber Institute) at Delft.

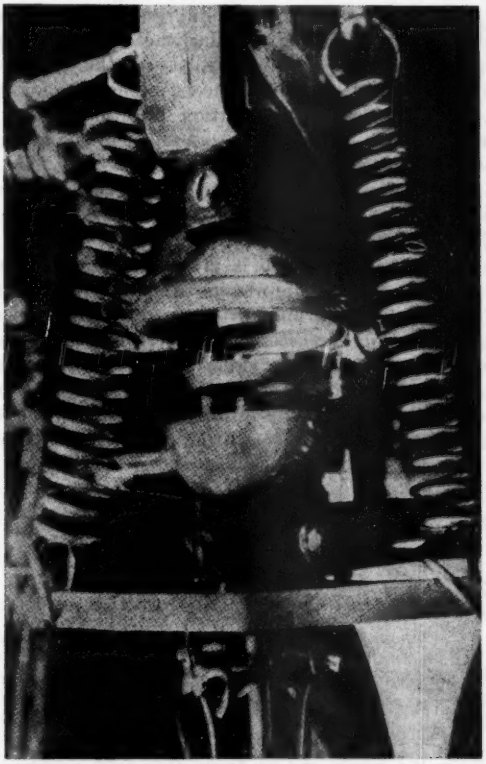

FIG. 1.—Steam-heated dies of steam-plastometer, showing extra feeler, that actuates the thickness gauge.

In this apparatus, heated with steam, a rubber specimen is compressed at 100° C by a die of 1 sq. cm. and a force of 10 kg. from 2 to 1 mm.; then the force is released and the thickness read to which the specimen recovers in 15 seconds. Part of the instrument, with the extra feeler, is shown in Figure 1. In this way, the determination of recovery takes less than 1 minute. No cigaret paper is to be used round the samples, as is recommended[3] for measuring plasticity, because for recovery the rubber has to stick to the dies. The two methods mentioned differ in two points. First, the temperature for the balance plastometer can be chosen at will, but was mostly taken at 70° C,

although the high-speed apparatus works at 100° C. Secondly, the first method compresses from 4 to 1 mm. before recovering, the second from 2 to 1 mm. This 2 mm. was taken because then a very short time for warming up is needed. It was found that taking 4 or 2 mm. for the initial thickness makes very little difference.

Both ways of measuring recovery, which are essentially the same, always begin with compressing to a certain extent and not for a certain time[4]. This way of measuring recovery is also preferred by Piper and Scott[5]. As has been indicated by Hoekstra[6], this method of measuring is thought advantageous over the other one, because when one compresses till a certain thickness is reached, relaxation in every case diminishes the elastic stresses to somewhat the same extent, independent of the plasticity of the rubber tested. For a hard sample shows a slow relaxation, but needs a long time for the compression, whereas a soft one shows strong relaxation but takes little time for compression. So in both cases relaxation has an effect of the same order.

Recovery and plasticity.—Having thus chosen the method of investigation and apparatus, the authors first wanted to decide whether recovery must be seen as a property correlated to plasticity or as something rather independent of the length of the rubber molecule.

It was found that the recovery of a given sample of rubber is influenced by the temperature at which compression and recovery takes place. If a given sample of raw rubber is masticated to different plasticities, recovery values are found indicating a *critical plasticity;* this critical plasticity gives a maximum of recovery. It must be stated that this critical value is a very undesirable plasticity in practice, since recovery in rubber manufacture is usually considered undesirable. This critical value is not the same for different temperatures of measuring. As is seen from Figure 2, the rate of recovery is

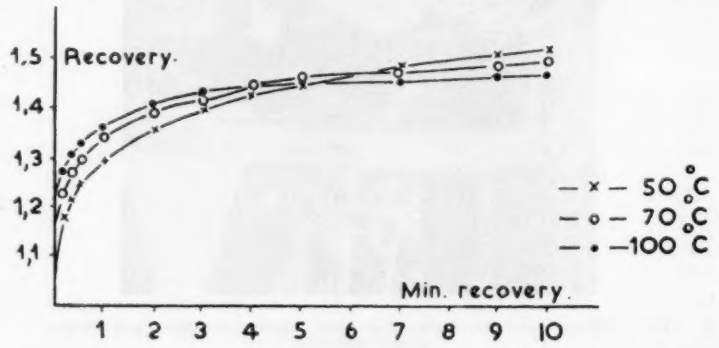

FIG. 2.—Recovery-time curves, taken from the same sample of rubber, masticated 15 minutes (see Figure 3); compression and recovery in the balance plastometer at 50°, 70° and 100° C.

much slower at a lower temperature; this is in accord with the higher inner viscosity of rubber at lower temperature. Apart from this, in the case of the rubber sample of Figure 2, recovery after 10 minutes was highest at the lowest temperature. This, as we said before, is not always the case (see Figure 3). For a plastometer temperature of 50°, the optimum of plasticity is D 1/4 of 0.2 or less. D 1/4 means the compression with 10 kg. with die of 1 sq. cm. during 15 seconds at 100° C. Measuring at 70° and 100° the critical value for this same series of masticated rubbers lies at other plasticities:

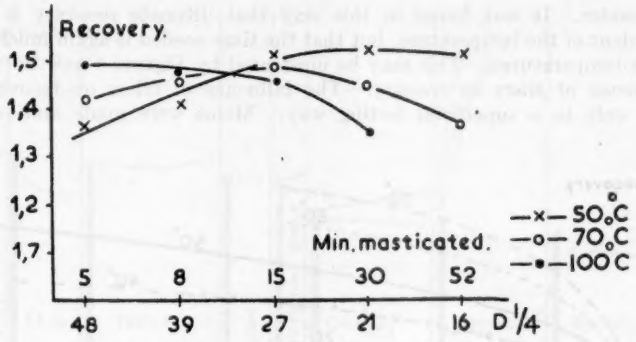

FIG. 3.—The recovery of samples of rubber, masticated for different times, was measured at three different temperatures. The maximum recovery lies at different plasticities but amounts in every case to 1.45–1.50.

TABLE 1

RECOVERY OF MASTICATED SHEET RUBBER AT CRITICAL PLASTICITY AT DIFFERENT TEMPERATURES

Temperature of measuring	Critical plasticity[7] D 1/4	Recovery
100°	0.2 –0.6	1.46–1.51
70°	0.25–0.3	1.45–1.49
50°	0.1 –0.2	1.50–1.52

One gets the impression that recovery when determined in this way is a property quite apart from plasticity, and not much influenced by mastication. This conclusion, of course, is a consequence of the particular test method, used by us, and cannot be applied to other test methods, for instance, the Defo test. When the temperature of mastication was raised it was found that recovery (as measured at 70°) was increased on prolonged mastication.

TABLE 2

INCREASE OF RECOVERY BY PROLONGED HOT MASTICATION

Time of hot mastication	D 1/4	Recovery
5 min.	0.51	1.36
15 min.	0.38	1.39
52 min.	0.25	1.45

It is not improbable that this effect of prolonged hot mastication is the same as the recovery-enhancing effect of hot storing[8].

Influence of the temperature at which recovery takes place.—In practice recovery occurs mostly at other temperatures than the deformation inducing it. Normally, recovery takes place at a lower temperature. We wanted to know what influence this change of temperature has on the speed and ultimate degree of recovery. Therefore, a loose metal disc of known thickness was placed on a sample of masticated rubber. Sample and disc were placed in the balance plastometer, compressed, and then quickly taken out with die and all and put in a constant temperature bath. By means of a system of levers inserted in this bath exact measurements of recovery were carried out with a horizontal microscope, fitted with cross-threads and a micrometer-screw and used as a

cathetometer. It was found in this way that ultimate recovery is almost independent of the temperature, but that the time needed is again much longer at lower temperatures. This may be illustrated by Figures 4 and 5.

Influence of fillers on recovery.—The influence of fillers on recovery was studied only in a superficial testing way. Mixes were made and recovery

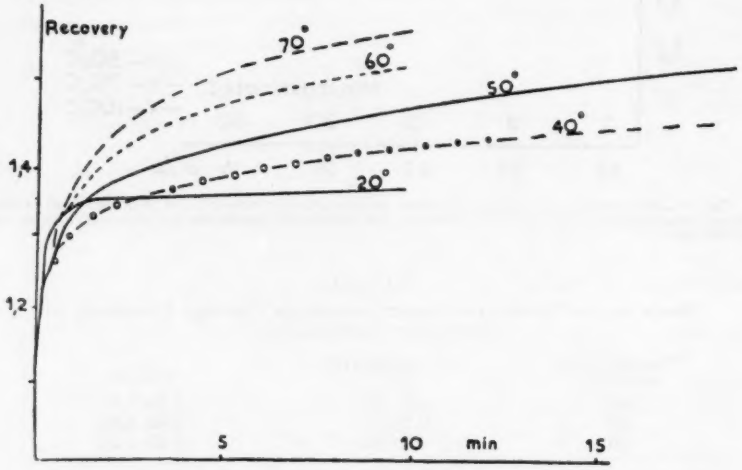

FIG. 4.—Recovery at different temperatures after compressing from 4 to 1 mm. at 70°.

determined; the same rubber was masticated without filler to the same plasticity as the mix, and recovery of this rubber was compared with that of the mixed stock. In every case recovery decreases with admixture of fillers. Attempting to determine a numeric value that would indicate the influence of fillers on the recovery of masticated rubber mixes, we divided the recovery of the mix by the recovery of the rubber alone.

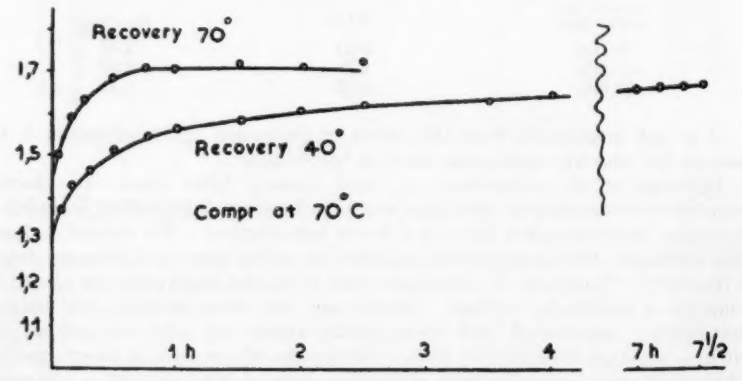

FIG. 5.—Ultimate recovery at 40 and 70° C of masticated rubber sheet, compressed from 4 to 1 mm. at 70° C.

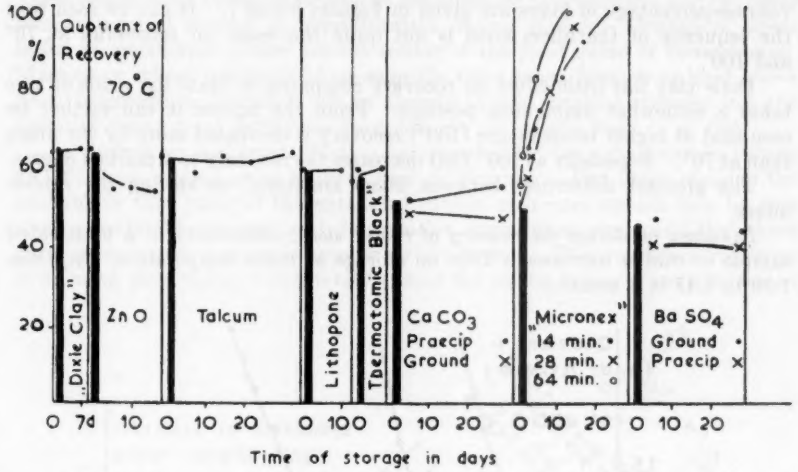

FIG. 6.—Quotients of recovery of rubber-filler mixes with 20 per cent by volume of filler, measured at 70° C immediately after mixing and after increasing times of storing at room temperature.

This quotient we called the *quotient of recovery*. It was not independent of the temperature at which determination of recovery took place. It is always less than one, and decreases with higher temperature of determination.

If one fixed temperature for the determination is chosen, a comparison between different fillers can be made. Results of mixes containing the same

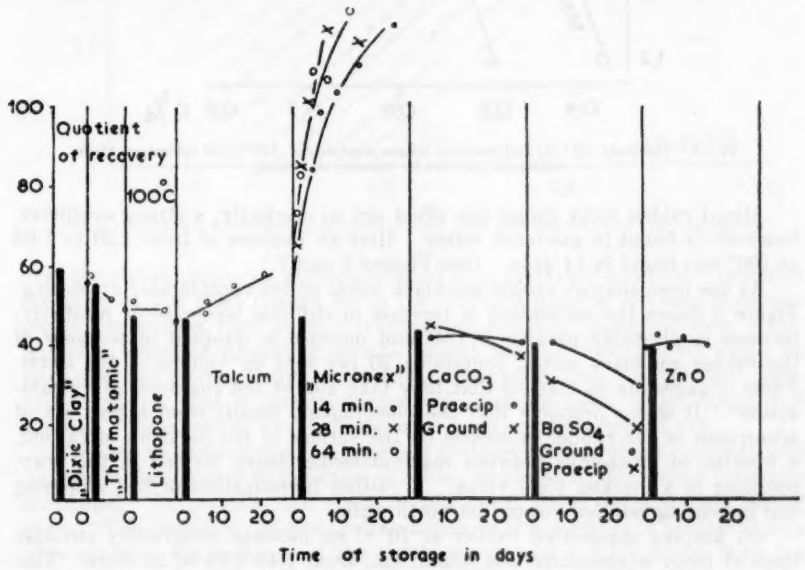

FIG. 7.—Quotients of recovery of rubber-filler mixes with 20 per cent by volume of filler, measured at 100° C immediately after mixing and after increasing times of storing at room temperature.

volume-percentage of fillers are given in Figures 6 and 7. It can be seen that the sequence of the fillers tried is not quite the same for recoveries at 70° and 100°.

Dixie clay has little effect on recovery compared to blanc fix; oxide of zinc takes a somewhat ambiguous position. From the figures it can further be seen that at higher temperature (100°) recovery is decreased more by the fillers than at 70°. Especially at 100° ZnO decreases the recovery to a marked degree.

The greatest differences between fillers are found on storing the rubber mixes.

Influence of storage on recovery of rubber stock.—Recovery of a masticated sample of rubber increases a little on storage at room temperature, *e.g.*, from 1.39 to 1.47 in 2 months.

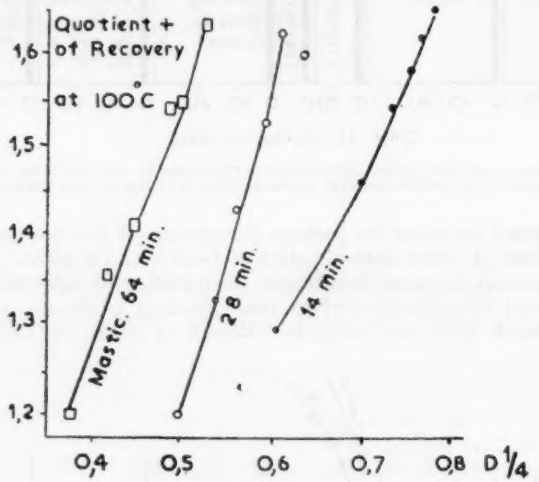

FIG. 8.—Plasticity (D 1/4) and recovery (steam plastometer, 100° C) of rubber-gas black mixes (20 per cent by volume) on storing.

Mixed rubber stock shows this effect not so markedly; a strong exception, however, is found in gas-black mixes. Here an increase of from 1.20 to 1.63 at 100° was found in 14 days. (See Figures 6 and 7.)

As has been shown[1], rubber gas-black mixes stiffen considerably on storing. Figure 8 shows the correlation of increase in stiffness (decrease in plasticity, increase in plasticity number D 1/4) and increase in quotient of recovery of the rubber gas-black mixes, containing 20 per cent by volume of the latter. These changes are so marked that they take almost the character of vulcanization[8]. It seems probable that the phenomenon results from a slow act of adsorption of the rubber molecules on the surface of the particles of carbon, a number of cross-links between macromolecules being formed in this way, resulting in a marked yield value. A further investigation of this stiffening and increasing resilience would be worth while.

On keeping masticated rubber at 70° C an increase remarkably stronger than at room temperature was found, *e.g.*, from 1.43–1.73 in 10 days. This increase was strongest in the case of rubber masticated for longer periods.

These effects must certainly be seen as the influence of orientation and (at lower temperatures of storing) of crystallization during storage. Centers of orientation in masticated rubber are the source of the yield value of this material. Masticated rubber has no yield value in the strict sense, because at least above room temperature slow flow sets in already at low shearing stresses; but the material shows great deviations from the law of viscous flow[7] ($\tau = D\eta$).

As there is no real crystallization (as recorded by x-ray diagram) in rubber at 70°, these centers must be very tiny or irregular. But there remains the probability that parts of the entangled rubber molecules remain side by side after considerable heating and deformation have taken place, and that these parts grow or even increase in number on hot storing. This increase in resilience or seeming yield value, which tends to lend the elastic behavior preponderance

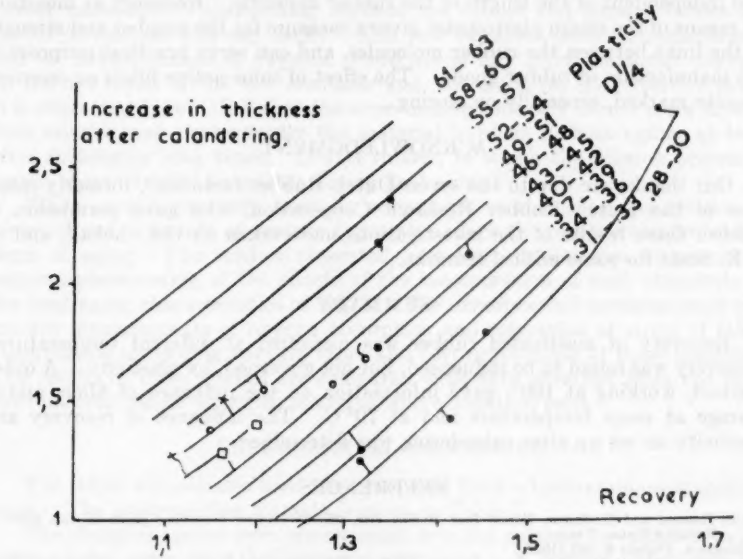

FIG. 9.—Increase in thickness of masticated rubbers (with and without filler) after calendering.

over the viscous behavior, is often referred to in literature as nerve. Probably the cause of this inner change lies in the fact that parts of the long molecules are slowly finding their most advantageous positions alongside each other. A certain effect of increasing specific weight should, therefore, be found on prolonged hot storing if the given explanation holds true. If not, the possibility remains, that a certain oxygen-vulcanization takes place during hot storing. These points, to our knowledge, have not been solved yet.

Recovery and calendering.—A practical problem for the rubber manufacturer consists in the increase in thickness of rubber stock after calendering[9] (calender shrinkage). In practice, the stock is calendered when hot and then cooled down. The conditions of this cooling influence this increase in thickness to a large extent. For instance, if the sheets are put on a table where they can stick to the surface, there is not much possibility to contract and increase the

thickness. If they are put on a surface well powdered with talc, they contract considerably.

A number of masticated rubbers were measured for plasticity and recovery. They were calendered in the same manner and deposited on a well powdered zinc table-top where they could shrink freely. The thickness was determined while the stock was on the calender rolls and once more after 20 minutes on the zinc table. The results are given in Figure 9 and indicate that the increase in thickness is indeed almost exclusively determined by the two factors: plasticity number and recovery. Therefore recovery determinations should be of a certain use in factory practice, when dealing with calendered goods[9].

Discussion of results.—Our investigation of recovery of masticated and mixed rubber leads to the conclusion that recovery is an independent property of masticated rubber, connected with the entanglement of rubber molecules and independent of the length of the rubber molecule. Recovery as measured by means of the steam plastometer gives a measure for the number and strength of the links between the rubber molecules, and can serve practical purposes in the manufacture of rubber goods. The effect of some active fillers on recovery is quite marked, especially on storing.

ACKNOWLEDGMENT

Our thanks are due to the seven Dutch Rubber factories[10], formerly members of the Dutch Rubber Research Coöperation, who gave permission to publish these results of the investigations undertaken on their behalf, and to J. R. Scott for some critical remarks.

SUMMARY

Recovery of masticated rubber was measured at different temperatures. Recovery was found to be influenced, but not governed, by plasticity. A quick method, working at 100°, gave information on the influence of fillers and of storage at room temperature and at 70° C. The influence of recovery and plasticity on set up after calendering was determined.

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EFFECT OF CHEMICAL AGENTS ON HEAT DETERIORATION OF GR-S *

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The oxidative deterioration of rubber at elevated temperatures is mainly the result of two concurrent processes[1]: (1) cross-linking and (2) scission of the rubber molecules. Cross-linking hardens the rubber and scission causes the rubber to become soft and tacky. The two reactions occur simultaneously, and the actual change in physical properties of any given elastomer depends on the net result of the two reactions and, therefore, on their relative rates. It is characteristic of GR-S that the cross-linking generally occurs more rapidly than scission and consequently the material hardens in heat aging, at least after sufficiently long times. (Butyl rubber, in which the scission process is faster, characteristically softens during heat aging.)

While oxygen generally must be present for cross-linking and scission to occur, chemical agents of various types also affect the reactions under conditions of aging. The studies presented here were undertaken to provide a better understanding of the effects of the incorporation of such chemicals on the heat aging characteristics of GR-S. The experimental methods employed involve measurements of oxygen absorption and relaxation of stress of GR-S vulcanizates containing varying types and (or) proportions of these materials. The results of these studies are compared with data obtained from the more conventional tensile strength, modulus, and elongation tests.

EXPERIMENTAL PROCEDURE

The GR-S vulcanizates used were prepared from a hydroquinone stabilized latex. The compounding formula is given in Table I.

The chemical agents were incorporated into the polymer by addition to the uncoagulated latex in a benzene soap emulsion. A control, containing no added chemical agent, was prepared also. A total of fifteen different chemical agents were studied. Their chemical and trade names are given in Table I. To simplify the presentation of data, only five of these chemical agents are considered in detail throughout this paper. The data for the remaining ten are summarized in Tables II to V. The five chemical agents to which particular emphasis has been given are PBNA, Santoflex-B, BLE, manganous naphthenate, and benzoyl peroxide. It is shown that the first three exhibit a beneficial action on the heat deterioration of GR-S and the latter two a deleterious action, when compared to the control.

Oxygen absorption measurements of the various vulcanizates were carried out at constant pressure in a static system. The apparatus employed has been previously described[2]. For the studies of continuous and intermittent stress relaxation a modified stress relaxometer was used[3]. The measurements of

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TABLE I

BASIC FORMULA FOR GR-S VULCANIZATES

Polymer	100.0
Sulfur	2.0
Zinc oxide	5.0
Stearic acid	0.3
Santocure	1.2
Bardol	5.0
Easy processing carbon black	50.0
Chemical agent	...

CHEMICAL AGENTS STUDIED[a]

1. PBNA	Phenyl-β-naphthylamine
2. Santoflex-B	2,2,4-Trimethyl-6-phenyl-1,2-dihydroquinoline
3. BLE	5,5-Dimethylacridane
4. Benzoyl peroxide	Dibenzoyl peroxide
5. Manganous naphthenate	....
6. Phenylhydrazine	....
7. Diphenylamine	....
8. Stalite	Heptylated diphenylamine
9. Stabilite Alba	*N,N'*-*o*-tolyl-ethylenediamine
10. TAPS	*p*-*tert*-Amylphenol sulfide
11. Ferrous naphthenate	....
12. Bardol	Neutral coal tar fraction
13. Paraffin	....
14. Piperidine	....
15. TJB	*N*-nitrosodiphenylamine
16. DDM	Dodecanethiol

[a] Many of these products are commercial mixtures in which the chemical named is one of the major constituents.

continuous relaxation were made at 130° and 100° C and at 50 per cent elongation. The intermittent measurements were made at 130° C only and at 30 per cent elongation. In all cases the temperature of the samples did not vary over ±0.3° C. Tensile strength, modulus, and elongation measurements were carried out in the conventional manner at the Akron laboratories of The Firestone Tire and Rubber Company.

EFFECT ON CONTINUOUS STRESS RELAXATION

The reactions of cross-linking and scission that occur simultaneously in rubber polymers at elevated temperatures may be separated and the relative extent of each studied independently by means of continuous and intermittent stress relaxation experiments. When a sample of rubber is extended to a fixed elongation and exposed to air at elevated temperatures, the relaxation of stress of the stretched sample measures the extent of scission that is occurring provided cross-linking is not too extensive. On the other hand, when the rubber sample is kept in a relaxed state and only stretched during short periodic measurements of the 30 per cent modulus, then the variation of stress with time measures the sum of both the cross-linking and scission reactions. For Hevea and Butyl rubbers, the stress, measured intermittently, decreases with time, whereas for GR-S the stress increases. Since both Hevea and Butyl rubbers become soft and tacky when exposed to air at elevated temperatures, whereas GR-S vulcanizates harden and become brittle, it is clear that the effect of the cross-linking reaction is greater than the scission reaction for GR-S and

TABLE II

STRESS RELAXATION AND OXYGEN ABSORPTION STUDIES

Added chemical agent (%)	Continuous stress relaxation				Intermittent stress relaxation		Oxygen absorption	
	$T_{0.50}$[a]	S/S_{min}[b]	T_{min}[c]	$T_{0.30}$[d]	$T_{1.5}$[e]	$T_{1.5}/T_{0.50}$	$k'_{02} \cdot 10^4$[f]	$k'_{02} \cdot T_{0.50} \times 10^4$
Control	0.67	0.05	12.5	74.0	8.5	12.6	1.07	0.71
PBNA								
0.5	0.96	0.045	17.0	85.0	15.0	15.7	0.72	0.69
1.0	1.10	0.044	17.0	85.0	16.0	13.6	0.63	0.69
2.0	1.35	0.04	17.0	90.0	22.0	16.3	0.62	0.84
Santoflex-B, 1.0	1.62	0.03	21.0	112.0	18.0	11.3	0.49	0.79
BLE, 1.0	1.10	0.050	29.0	147.0	17.0	13.6	0.54	0.60
Manganous naphthenate, 2.0	0.65	0.10	10.5	37.0	6.4	10.0	1.06	0.69
Benzoyl peroxide, 2.0	0.43	0.140	6.0	27.0	5.6	14.0	1.97	0.85
Ferrous naphthenate, 2.0	0.80	0.138	10.5	38.0	8.0	10.0	0.98	0.78
Bardol, 2.0	0.66	0.090	8.5	35.0	8.4	12.7	1.02	0.68
Paraffin, 2.0	0.57	0.07	8.6	48.0	8.0	14.0	1.15	0.66
Paraffin, 5.0	0.45	0.085	7.9	33.5	7.3	16.2	1.52	0.68
Phenylhydrazine, 2.0	0.93	0.048	13.0	66.0	13.0	15.0	0.76	0.70
1.0% PBNA (accelerator omitted)	2.0	0.040	19.0	88.0	14.0	7.0	0.35	0.70
Stabilite Alba, 1.0	0.89	0.03	13.8	70.0	10.0	11.2	1.02	0.91
Diphenylamine, 1.0	0.78	0.058	9.5	74.0	8.5	10.9	0.98	0.76
Piperidine, 2.0	0.82	0.028	12.5	71.0	11.0	13.4	0.94	0.77
DDM, 2.0	0.70	0.028	10.6	50.0	9.5	13.5	1.16	0.81
Stalite, 1.0	0.96	0.045	21.0	100.0	16.0	16.6	0.54	0.52
TJB, 0.4	0.53	0.028	11.0	48.0	9.1	17.2	0.71	0.38

[a] $T_{0.50}$ = Time required (hours) for stocks to relax to 0.5 of initial stress.
[b] Value of stress divided by initial stress at minimum point in relaxation curve.
[c] Time required (hours) for stress to relax to its minimum value.
[d] Total time required (hours) for stock to attain 0.30 times initial stress after passing minimum stress value.
[e] Time required (hours) for stress to increase to 1.5 the initial value.
[f] Calculated from total amount of oxygen absorbed during initial 8 hours and in units of moles of oxygen absorbed per gram rubber vulcanizate per hour.

TABLE III

$T_{0.50}$	S/S_{0min}	T_{min}	$T_{0.90}$	$T_{1.5}$	k'_{02}
CHEMICAL AGENTS EXHIBITING BENEFICIAL ACTION ON PROPERTIES OF GR-S VULCANIZATES					
1. No accelerator + PBNA	1–3. TJB, DDM, and Piperidine	1. BLE	1. BLE	1. PBNA	1. No accelerator + PBNA
2. Santoflex-B	4–5. Santoflex-B and Stabilite Alba	2–3. Santoflex-B and Stalite	2. Santoflex-B	2. Santoflex-B	2. Santoflex-B
3. PBNA	6. PBNA	4. No accelerator + PBNA	3. Stalite	3. BLE	3–4. BLE and Stalite
4. BLE		5. PBNA	4. PBNA	4. Stalite	5. PBNA
5. Stalite			5. No accelerator + PBNA	5. No accelerator + PBNA	
CHEMICAL AGENTS EXHIBITING DELETERIOUS ACTION ON PROPERTIES OF GR-S VULCANIZATES					
1. Benzoyl peroxide	1. Benzoyl peroxide	1. Benzoyl peroxide	1. Benzoyl peroxide	1. Benzoyl peroxide	1. Benzoyl peroxide
2. Paraffin	2. Ferrous naphthenate	2. Paraffin	2. Paraffin	2. Manganous naphthenate	2. Paraffin
3. TJB	3. Manganous naphthenate	3. Bardol	3. Bardol	3. Paraffin	3. Manganous naphthenate
4. Manganous naphthenate	4. Bardol	4. Manganous naphthenate	4. Manganous naphthenate	4. Ferrous naphthenate	4. Bardol
5. Bardol	5. Paraffin	5. Ferrous naphthenate	5. Ferrous naphthenate	5. Bardol	5. Ferrous naphthenate

TABLE IV

Unaged/Aged 200% modulus	Aged/Unaged tensile strength	Aged/Unaged elongation at break
CHEMICAL AGENTS EXHIBITING BENEFICIAL ACTION ON PROPERTIES OF GR-S VULCANIZATES		
1. Piperidine	1. Paraffin	1. Piperidine
2. No accelerator + PBNA	2. No accelerator + PBNA	2. Phenylhydrazine
3. PBNA	3. Piperidine	3. No accelerator + PBNA
4. Stabilite Alba	4. Bardol	4. BLE
5. Santoflex-B	5. BLE	5. Santoflex-B
CHEMICAL AGENTS EXHIBITING DELETERIOUS ACTION ON PROPERTIES OF VULCANIZATES		
The 200% modulus of the following stocks could not be measured	1. Manganous naphthenate	1. Manganous naphthenate
	2. DDM	2. Benzoyl peroxide
Phenylhydrazine		
Stalite	3. Benzoyl peroxide	3. DDM
Ferrous naphthenate		
TJB	4. TJB	4. Ferrous naphthenate
Manganous naphthenate		
Paraffin	5. PBNA	5. Diphenylamine
Benzoyl peroxide		
Diphenylamine		

TABLE V

Chemical agents causing high unaged tensile	Chemical agents causing high elongation at break	Chemical agents causing high unaged modulus
1. DDM	1. DDM	1. Piperidine
2. PBNA	2. Bardol	2. Stabilite Alba
3. Control	3. PBNA	3. PBNA
4. BLE		4. Diphenylamine
5. Santoflex-B		
Chemical agents causing low tensiles	**Chemical agents causing low elongation at break**	**Chemical agents causing low unaged modulus**
1. Paraffin	1. Piperidine	1. Bardol
2. No accelerator + PBNA	2. Manganous naphthenate	2. DDM
3. Manganous naphthenate	3. Phenylhydrazine	3. TJB
4. Piperidine	4. Ferrous naphthenate	4. No accelerator + PBNA
5. Benzoyl peroxide	5. Paraffin	5. Paraffin

vice versa for Hevea and Butyl. (Hevea rubber becomes hard and brittle after prolonged aging at elevated temperatures.)

The effect of the addition of beneficial and deleterious chemical agents into GR-S vulcanizates as measured by the rate of continuous stress relaxation is shown in Figures 1 and 2. In every case stress divided by initial stress is plotted against logarithmic time. It is evident that at both temperatures the two deleterious chemical agents accelerate the rate of scission when compared to the control. On the other hand, the three beneficial chemical agents PBNA,

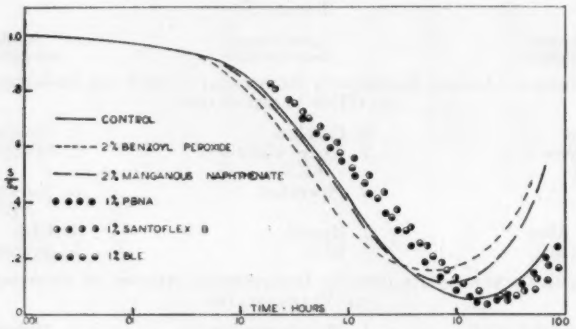

FIG. 1.—Effect of chemical agents on stress relaxation, GR-S at 130° C.

Santoflex-B, and BLE (commonly used as antioxidants) may be observed to retard the rate of chain scission. In all cases, similar trends are noted among the different chemical agents at 100° and 130° C, although the entire aging process is accelerated at the higher temperature. The reproducibility of two duplicate relaxation runs for manganous naphthenate and BLE is shown in Figure 3. Samples are from the same mix and cure but previous experience[4] suggests that nearly the same reproducibility could be obtained from completely independent samples.

The 130° C continuous stress relaxation experiments were carried out for a sufficient length of time (at least 72 hours) to observe the region where the

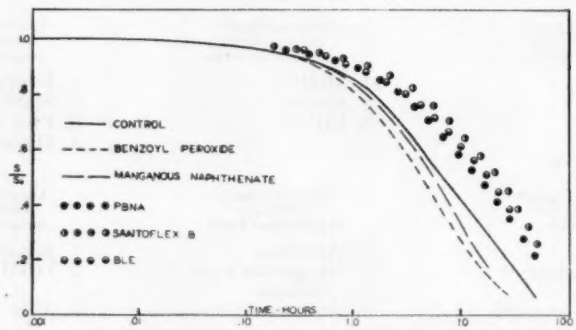

FIG. 2.—Effect of chemical agents on stress relaxation, GR-S at 100° C.

stress, having once reached a minimum value, begins to increase with time. This phenomenon, which produces the appearance of a tail near the end of each relaxation curve, is reproducible in duplicate runs with the same accuracy as in the part of the relaxation curve where the stress decreases.

The explanation for this increase of stress which first suggested itself was that the method of measuring the stress might be responsible: The band is actually extended very slightly beyond 50 per cent, an amount just sufficient to cause a flicker in a contact connected to a lower pulley. When the rubber sample becomes extremely hard, even though the stress has decayed almost completely to zero at precisely 50 per cent elongation, it is necessary to work

against the modulus in taking the stress reading, which might give the appearance of a sizable stress. This hypothesis may be subjected to test by running a duplicate sample in a tilting relaxometer[5]. The method of measuring the stress is different in this apparatus: To cause a flicker in the signal light, the rubber band must draw itself back slightly from its fixed 50 per cent elongation. Thus if the stress actually were decaying to zero at precisely 50 per cent elongation, the sample would not be able to draw itself to less than 50 per cent elongation, and the stress should decay completely to zero when measured in this apparatus. An examination of the two curves in Figure 4 shows that the

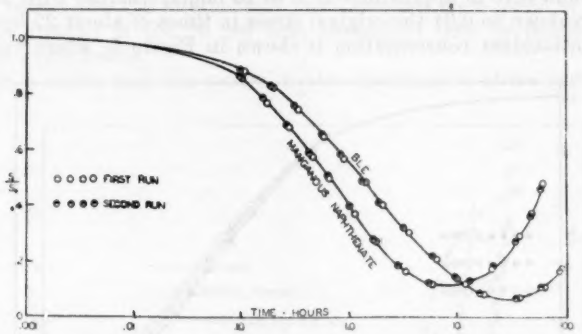

FIG. 3.—Effect of chemical agents on stress relaxation, duplicate runs.

stress does not decay to zero when measured in the tilting apparatus, but follows the stress increase of the sample measured in the standard apparatus closely, the minimum stress value being duplicated exactly in the two curves. In view of this result and other similar studies, it seems certain that this observed increase of stress is a true effect and is not due to the method of stress measurement.

The explanation which seems most reasonable at the present time is that an increased concentration of cross-links (or perhaps extensive cyclization) actually causes a shrinkage of the rubber sample, and when this becomes sufficiently pronounced the resulting tensile contracting force in a rubber

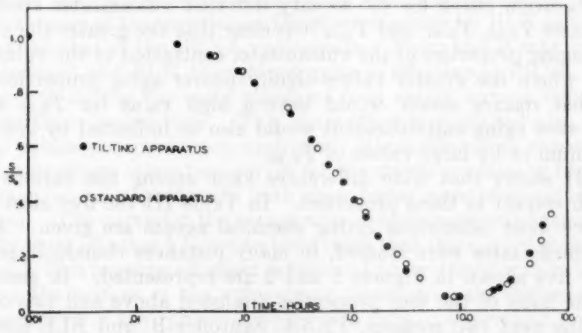

FIG. 4.—Apparatus cross check.
Stress relaxation, GR-S at 130° C, phenylhydrazine.

sample being held at a fixed elongation causes an increase in the observed stress. The GR-S samples studied were hardening considerably at the time at which the stress increase was noticed. One GR-S sample broke while standing in the oven, after about 1 week at 130° C; the internal stress apparently had become great enough to break the sample (at the last reading, the stress had already increased to over 0.6 of the initial stress in this sample).

The times at which the minimum value of stress is reached vary among the vulcanizates containing different chemical agents. Samples containing benzoyl peroxide or manganous naphthenate, for example, reach a minimum stress value of about 0.10 in approximately 6 to 10 hours, whereas BLE and Santoflex-B relax down to 0.04 the original stress in times of about 22 hours. The effect of antioxidant concentration is shown in Figure 5, where vulcanizates

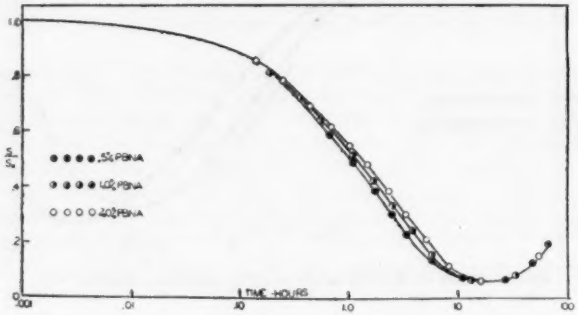

FIG. 5.—Effect of chemical agent on stress relaxation, GR-S at 130° C.

compounded with 0.5, 1.0, and 2.0 per cent PBNA are observed to relax initially at rates which depend on the amount of chemical agent present—that is, the stock containing 2.0 per cent PBNA relaxed slower than the stock containing 0.5 per cent, while the 1.0 per cent PBNA stock was intermediate. After a time of 17.0 hours, however, all samples reached the same minimum stress value of 0.04, whereupon their rates of increase of stress with time proceeded with no appreciable difference.

Table II was compiled to indicate the outstanding features of each continuous relaxation curve for the twenty different vulcanizates studied. For the three cases $T_{0.50}$, $T_{0.30}$, and $T_{\min}$ it is clear that the greater the values, the better the aging properties of the vulcanizate, contrasted to the values of S/S_0 minimum, where the greater values signify poorer aging properties. A vulcanizate that relaxes slowly would have a high value for $T_{0.50}$ and $T_{\min}$. Relatively slow aging embrittlement would also be indicated by low values of S/S_0 minimum or by large values of $T_{0.30}$.

Table II shows that wide differences exist among the various chemical agents with respect to these properties. In Table III the five most beneficial and the five most deleterious acting chemical agents are given. As twenty different vulcanizates were studied, in many instances chemical agents other than those five shown in Figures 1 and 2 are represented. In general, however, on the basis of the four properties discussed above and two others discussed in the next two sections, PBNA, Santoflex-B, and BLE appear most beneficial, while benzoyl peroxide and manganous naphthenate appear most deleterious.

EFFECT ON INTERMITTENT STRESS RELAXATION

Due to the heat hardening action of GR-S the values obtained by plotting stress divided by initial stress from intermittent relaxation measurements increase with time, after a slight initial drop. In Figure 6 the effect of the addition of chemical agents into GR-S vulcanizates as measured by the rate of intermittent stress relaxation at 130° C is shown. These studies were not carried out for longer periods of time than 24 hours, and in the cases where a chemical agent had a deleterious effect, for only 10 hours, because the rubber samples had a tendency to break on being elongated after aging at 130° C. For this reason also the intermittent measurements were made at 30 per cent elongation instead of the 50 per cent elongation used in continuous stress relaxation experiments.

Figure 6 shows that the control rubber increases in stress faster than the

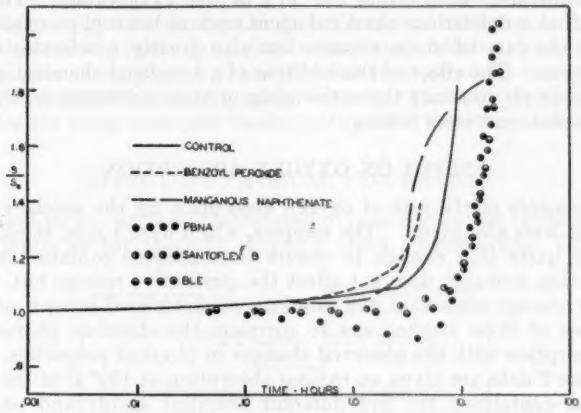

FIG. 6.—Effect of chemical agents on intermittent stress relaxation, GR-S at 130° C.

three vulcanizates containing 1 per cent PBNA, Santoflex-B, or BLE. Although the vulcanizates containing BLE or Santoflex-B increase in stress more rapidly than the PBNA vulcanizate during the early part of the experiment, in the later stages of the experiment the stress increase for BLE and Santoflex-B is slower than that of the PBNA vulcanizate. From this it may be concluded that Santoflex-B and BLE, though not quite so effective as PBNA in retarding embrittlement during the early stages of heat aging, have a beneficial effect which lasts for a longer time. This same effect is exhibited also in the T_{min} and $T_{0.30}$ values obtained from continuous stress relaxation experiments.

The intermittent relaxation curves for the stocks containing benzoyl peroxide and manganous naphthenate both show faster rates of stress increase than the control. The curve for the manganous naphthenate vulcanizate, however, appears to level off after 5 hours to the extent that there is little stress increase with time. This leveling off effect is believed to be due to a thin, hard coating formed on the surface of the vulcanizate, preventing the diffusion of oxygen to the inner core of the rubber sample. (In oxygen absorption measurements it has been noticed also that this same vulcanizate after a rapid initial absorption of oxygen, absorbed little oxygen after 8 hours.) The presence of the

hard protective coating on the manganous naphthenate vulcanizate was actually observed, since the sample, on stretching, appeared to crack on the surface, exposing an inner core that was still quite elastic. The stock containing benzoyl peroxide aged noticeably, resembling manganous naphthenate. No leveling off effect could be observed, however, since the stock broke on elongating after 6 to 7 hours of aging. On the other hand, for the majority of the stocks studied, the 1-mm. thickness of the samples seemed thin enough to give homogeneous oxidation, so far as could be determined from visual inspection.

In Table II the intermittent stress relaxation experiments show fourfold variation: the stock containing benzoyl peroxide had a $T_{1.5}$ value of 5.6 hours, and therefore showed the most rapid hardening; the stock containing 2 per cent PBNA with a $T_{1.5}$ value of 22 hours obviously hardened least rapidly. The ratio of $T_{1.5}$ to $T_{0.50}$ (continuous stress relaxation) exhibits a much higher degree of constancy than either the $T_{1.5}$ or the $T_{0.50}$ values. Thus it was concluded that a deleterious chemical agent such as benzoyl peroxide not only accelerates the rate of chain scission but also greatly accelerates the cross-linking process. The effect of the addition of a beneficial chemical agent such as PBNA is simply to retard the entire aging process as determined by the rates of chain scission and cross linking.

EFFECT ON OXYGEN ABSORPTION

Measurements of the rate of oxygen absorption by the specially prepared vulcanizates were also made. The samples, which were 1 mm. thick, were not in all cases quite thin enough to ensure homogeneous oxidation at 130° C. This limitation probably does not affect the qualitative ratings but, in certain cases, may change somewhat the absolute magnitude of oxygen absorption. The purpose of these studies was to correlate the chemical phenomenon of oxygen absorption with the observed changes in physical properties.

In Figure 7 data are given on oxygen absorption at 130° C of the six GR-S vulcanizates containing the five different chemical agents and one control.

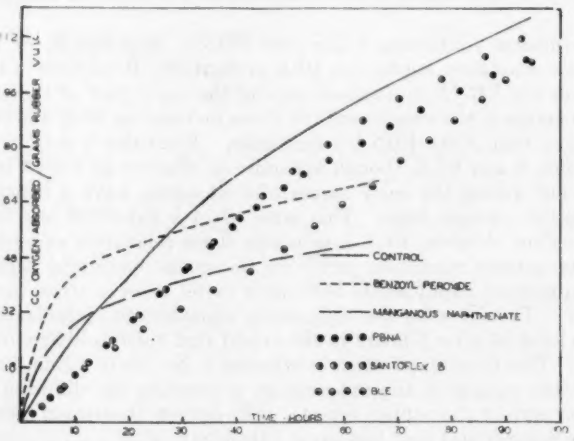

FIG. 7.—Effect of chemical agents on oxygen absorption, GR-S at 130° C.

In all cases the amount of oxygen absorbed per gram of rubber vulcanizate is plotted against linear time.

The presence of PBNA, Santoflex-B, and particularly BLE in the vulcanizate was effective in retarding the rate of oxygen uptake as compared to the control.

The vulcanizates containing benzoyl peroxide and manganous naphthenate initially absorbed oxygen much faster than the control. After approximately 8 hours, the rate of oxygen uptake for these two stocks began to decrease more rapidly than the control. This effect was most pronounced for manganous naphthenate inasmuch as after 8 hours the vulcanizate absorbed only a small amount of oxygen. The explanation for the leveling off effect due to retardation of diffusion as previously noted from intermittent stress relaxation studies is applicable here also.

The rate of oxygen uptake (k'_{0_2}) of the various stocks in moles of oxygen per gram of rubber vulcanizate per hour is shown in Table II. The values represent the average rate during the first 8 hours of oxidation. The values for the product of k'_{0_2} times $T_{0.50}$ show a constancy which indicates that the number of moles of oxygen per gram of vulcanizate required to cut half the original network chains at this temperature is nearly the same for all the stocks. These studies are being continued to elaborate on the theoretical interpretation of this fact.

EFFECT ON PHYSICAL PROPERTIES

In addition to the stress relaxation and oxygen absorption studies, physical tests were made on the specially prepared GR-S vulcanizates. In Figure 8

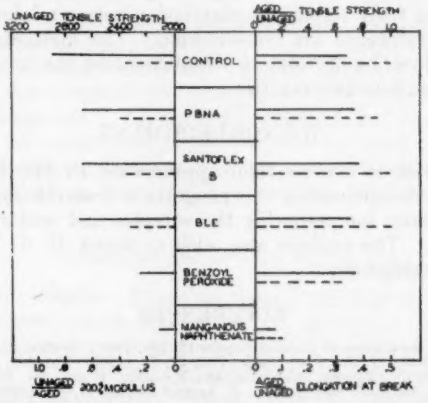

FIG. 8.

bar graphs represent four physical properties of the vulcanizates: unaged tensile strength; unaged/aged 200 per cent modulus; aged/unaged tensile strength; and aged/unaged elongation at break. The properties listed on top of the graph are the solid lines and the properties listed on the bottom, the broken lines. The longer the lines appear on the bar graphs the better are the listed aged properties. Although the unaged tensile strength does not represent any aging property of the vulcanizate, it exhibits the changes that occur

in the stock when cured with the different chemical agents. PBNA and dodecanethiol, for example, produce vulcanizates with high tensile strengths, while benzoyl peroxide and manganous naphthenate bring about low tensile strengths.

The aged/unaged tensile strength and elongation of break data were obtained by dividing the values after 96 hours aging at 100° C by the unaged values, and vice versa for the unaged/aged 200 per cent modulus. (In the latter case the unaged/aged modulus was evaluated since the 200 per cent modulus increases with aging. In some cases the samples broke before measurements could be made.) The best aging results are obtained from vulcanizates containing PBNA, Santoflex-B, and BLE. The poorer aging properties are shown by vulcanizates containing manganous naphthenate or benzoyl peroxide.

Table IV shows the standard aging properties of unaged/aged 200 per cent modulus, aged/unaged elongation at break, and aged/unaged tensile strength. In Table V the list is based on the first five chemical agents causing the highest and the lowest tensiles, elongations, and 200 per cent modulus in the unaged vulcanizates.

CONCLUSIONS

A detailed study of Tables III and IV, in which the effect of chemical agents on high temperature aging are evaluated by relaxation and oxygen absorption indexes and conventional test indexes, shows a much higher evaluation consistency for the Table III indexes and presents some doubt regarding the significance of the data given in Table IV and Figure 8. Although the conventional tests have the advantage of speed and convenience, the difficulties of obtaining truly significant correlation between laboratory aging tests and practical performance are considerable. The methods reported in this paper may, therefore, be of value in supplementing the numerous aging tests already in use in various laboratories.

ACKNOWLEDGMENT

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PLASTICIZERS FOR POLAR SYNTHETIC RUBBERS *

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One of the most useful methods of compounding natural or synthetic rubbers has been by the use of auxiliary materials known as plasticizers. These materials have been employed in rubber compositions for two broad general purposes: (1) to facilitate processing of the uncured rubber stock by softening the composition, increasing its plasticity, decreasing nerve, etc., and (2) to alter the properties of the final cured product by decreasing hardness, by lowering brittle temperature, by improving resistance to tear, or by other effects of similar character.

These two effects of plasticizer addition are corollary. However, certain specific groups of materials have pronounced effects on one type, but only a minor influence on the other group of properties.

Commercial materials of this general type were identified for many years merely as softeners. Many of the products employed in the rubber industry were complex chemical mixtures, often of varying composition. Until the advent of Neoprene synthetic rubber, there was little need for softeners or plasticizers, as they began to be known, which would be especially suitable for use with a particular polymer.

The development of plasticizers, particularly the ester types, for use with the newer thermoplastics has taken place largely within the past ten years. The commercial application of several types of synthetic rubbers of varying chemical structure and of specific physical and chemical properties has paralleled the plasticizer development. The successful utilization of these special-purpose synthetic rubbers for many product applications has been determined by the availability of the correct plasticizers which would so modify the properties of the original polymers as to make them suitable for the particular uses in question.

INFLUENCE OF POLYMER

Types of synthetic rubbers.—There are several methods of classifying natural and synthetic rubbers, which depend on the particular problem involved. For the purposes of this discussion, it is convenient to group these polymers into two general classes: those containing essentially no polar centers, and those containing significant proportions of polar groups or atoms. The nonpolar group would contain natural rubber as well as the synthetic hydrocarbon polymers—polyisoprene, polybutadiene, Butyl rubber, GR-S, etc. The polar group would contain the chloroprene polymers and copolymers (Neoprene), the nitrile rubbers (acrylonitrile-diene copolymers, etc.), acrylate-diene copolymers, chlorostyrene-diene copolymers, and numerous other polymers and copolymers containing polar atoms or groups such as Cl, CN, COOR, and F.

The mechanism of plasticizer action may involve either polar or nonpolar

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portions of the molecule, where both are present. Where only a nonpolar polymer is involved, the mechanism of plasticization is much simpler from thermodynamic considerations, inasmuch as secondary dipole linkages are not involved. For this and other considerations, it has been deemed wise to limit this treatment of the subject to those polymers possessing original polarity—that is, in the uncured state. It should be borne in mind that the vulcanization process as normally carried out produces dissymmetry (polarity) in the molecule, so that there are essentially no nonpolar polymers in the vulcanized state.

Polymer structural variations.—There are some regions of similarity in plasticization of the polar synthetic rubbers and the analogous polar thermoplastics. However, some structural modifications are possible in the synthetic rubbers which are not possible in the simpler polymer molecules, and therefore it is natural to expect that the problems associated with plasticization would be somewhat more complex.

The actual degree of polarity of the polymers will be determined first by the selection of the polar group and second by the fractional occurrence of this group in the molecule. Where the polar group is present in the monomer—for example, acrylonitrile—its occurrence in a copolymer depends on the relative rates of polymerization of the monomers and the degree of conversion of the combined monomers. The series of commercially available butadiene-acrylonitrile copolymers has a range of initial butadiene to acrylonitrile ratios from 85 to 15 to 55 to 45.

Other structural factors which determine to a great extent the behavior of the rubber with plasticizers are the molecular-weight distribution of the various polymer species; degree of linearity of the polymer—for example, 1,2- against 1,4- addition—and resultant crystallinity in the case of certain synthetic rubbers such as Neoprene; separation of chains by bulky substituents, such as methyl groups, benzene rings, etc.; and combination in the polymer chain of residues from certain polymerization ingredients (catalysts, chain transfer agents). It is also possible to introduce polar centers at various points in the polymer structure by after-treatment with various reagents such as halogens.

In addition to the structural features inherent in the original polymer, there are effects produced by various additives to the compounded rubber stock. The most outstanding of these is the effect produced by carbon black in reinforcement of the rubber. The mechanical effects produced by this type of material are pronounced, and they determine in many cases the need for plasticizer as well as its specific effects.

The vulcanization process introduces additional structural changes into the polymer molecule. The exact character of these changes has been the subject of a large amount of research. It is believed by many that the primary reaction is one of cross-linkage between adjacent polymer chains, and that the effects on mechanical properties are the result of the extent of cross-linkage. This general belief is substantiated by the excellent work of Flory[1] on Butyl rubber. On the other hand, Farmer has shown with materials of greater unsaturation[2] that cyclization can occur readily. The work of Stiehler and Wakelin[3] led them to the belief that the introduction of polar centers into the polymer molecule was the primary effect and that the mechanical properties of the vulcanized product were the result of polar bonding between adjoining polymer molecules. Although the exact nature of the vulcanized rubber structure may still not be clarified completely, it can at least be stated that the

vulcanized rubber consists of a network of tangled polymer chains, which are bound together in some fashion at various points of contact. The effectiveness of a plasticizer is a measure of the degree to which it modifies this network structure.

The effects of oxidation and other factors involved in the aging of a rubber product also are important in determining the apparent effects of plasticizers after such aging has taken place. This factor is one which has been overlooked by many workers in this field.

EFFECTS PRODUCED BY PLASTICIZERS

Effects in uncured rubber.—The effectiveness of plasticizers in uncured rubber stocks may be exhibited in several different ways.

Increased plasticity may allow milling or mixing operations to proceed more smoothly. Typical effects on plasticity are shown in Figure 1. In many instances it is difficult to incorporate pigment into the stock without the assistance of plasticizer. In other cases the nerve of the rubber is reduced so

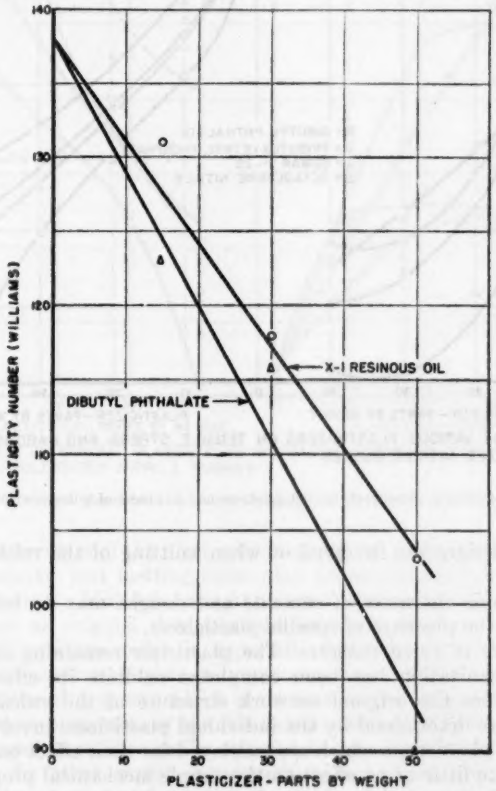

FIGURE 1. EFFECT OF TYPICAL PLASTICIZERS ON PLASTICITY OF A NITRILE RUBBER

FIG. 1.—Effect of typical plasticizers on plasticity of a nitrile rubber.

that it can be banded on the mill. An economic effect produced by plasticizers is a reduction in power consumption and often in mixing time.

Alteration of the elastic-plastic deformation ratio has significant effects in processing operations such as extrusion or calendering. It is possible by suitable plasticization to control such items as speed of extrusion, calender shrinkage, grain, dimensional stability, etc. Many of these processing operations can be carried out at lower temperatures with plasticized stock, thus minimizing the effects of scorch (precure).

Modification of the deformation characteristics of the rubber has a profound influence on the molding characteristics of the stock, especially when

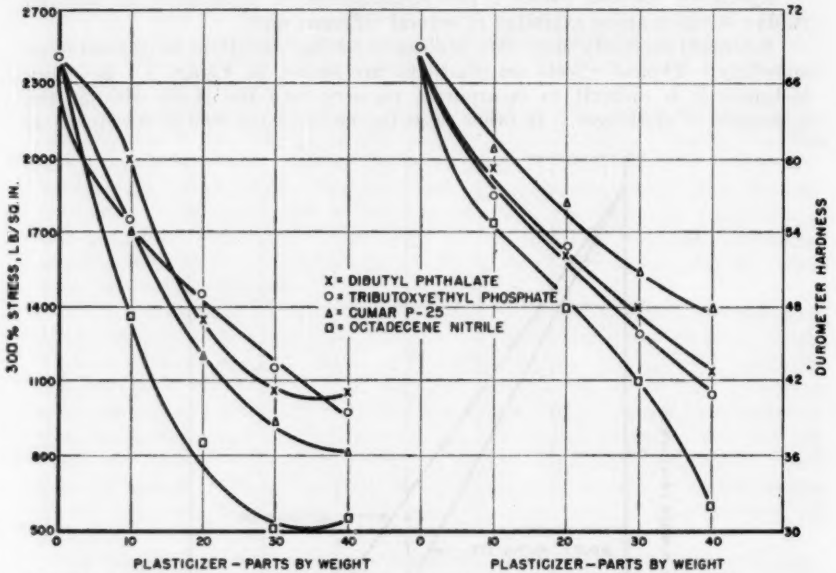
300% STRESS, LB/SQ. IN.
DUROMETER HARDNESS
X = DIBUTYL PHTHALATE
O = TRIBUTOXYETHYL PHOSPHATE
Δ = CUMAR P-25
□ = OCTADECENE NITRILE
PLASTICIZER – PARTS BY WEIGHT
PLASTICIZER – PARTS BY WEIGHT

FIGURE 2. EFFECT OF VARIOUS PLASTICIZERS ON TENSILE STRESS AND HARDNESS OF VULCANIZED NITRILE RUBBER

FIG. 2.—Effect of various plasticizers on tensile stress and hardness of vulcanized nitrile rubber.

intricate mold designs are involved or when knitting of the rubber stock is a problem.

The thixotropic character of cements and doughs may be influenced to a great extent by the presence of specific plasticizers.

General effects in cured rubbers.—The plasticizer remaining in the rubber stock after vulcanization has been completed exhibits its effects primarily because it modifies the original network structure of the vulcanizate. The specific effects are determined by the individual plasticizers involved.

Many of the plasticizers which are employed for their effect on the uncured rubber stock have little or no effect on the simple mechanical properties of the vulcanizate. Those materials which affect the finished product in general:

Decrease hardness and elastic modulus.

Increase elongation (this is true only within certain practical limits).

Produce a variable effect on tensile strength, resilience, tear resistance, and permanent set.

Produce a variable effect on the rate of curing.

Influence aging properties (the volatility of the plasticizer and its tendency toward oxidation are important factors).

Improve low-temperature flexibility in some cases and harm it in others (a limiting factor is the polymer in this instance).

Have variable effects on swelling properties of the composition.

Some of these properties are illustrated in Figures 2 to 4.

Specific properties of plasticizer.—Plasticizers are usually evaluated in terms of the effects which they produce. However, these in turn depend on certain

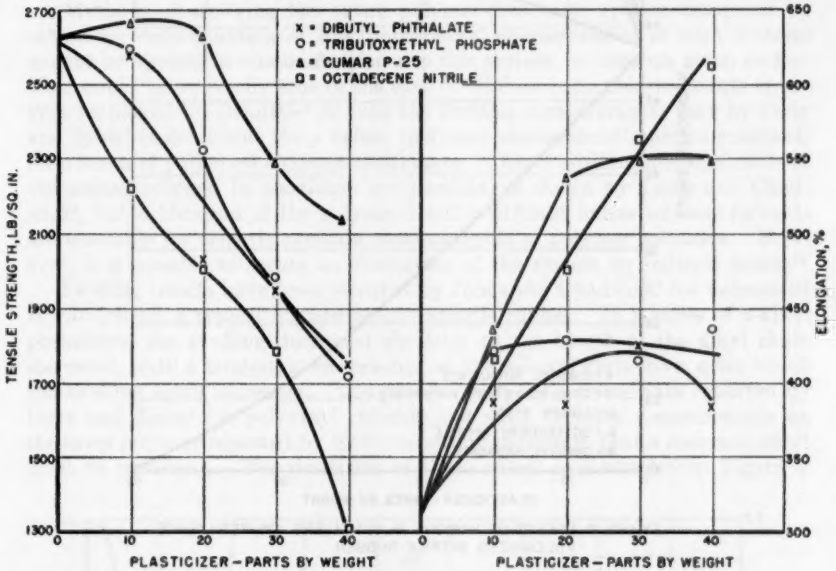

FIGURE 3. EFFECT OF VARIOUS PLASTICIZERS ON TENSILE STRENGTH AND ELONGATION OF A VULCANIZED NITRILE RUBBER

FIG. 3.—Effect of various plasticizers on tensile strength and elongation of a vulcanized nitrile rubber.

specific characteristics of the plasticizers themselves. Such properties as vapor pressure, viscosity, and melting point play an important part in determining ultimate behavior. Molecular weight and molecular structure of the plasticizer are important as original determinants for some of these properties. The shape of the plasticizer molecule, especially the shape which it assumes in the plasticized composition, is also an important characteristic[4].

Another type of property which is essentially derived from combinations of the above direct properties of the plasticizer, but which also reflects the character of the polymer, is usually referred to as compatibility, sometimes as miscibility[5]. In other words, compatibility is not an absolute property of either polymer or plasticizer, but is a result of the specific combination of materials.

Similar is another property which has been considered in detail for certain

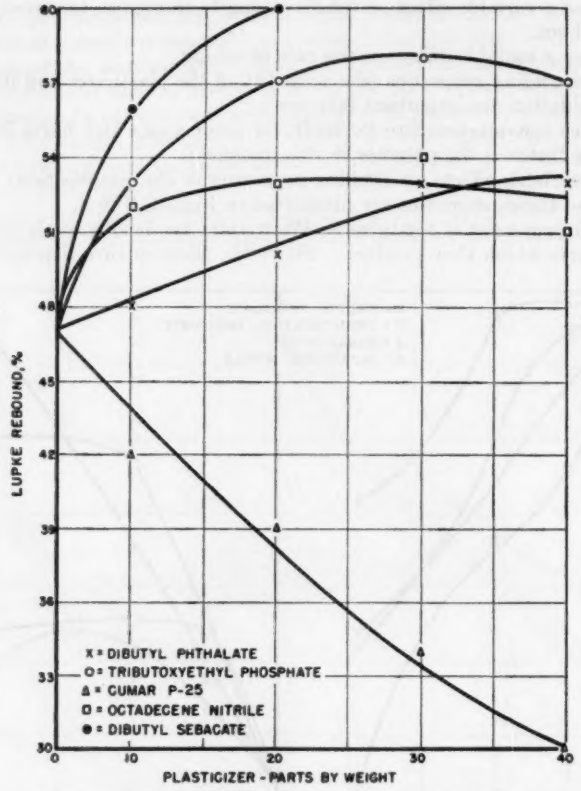
LUPKE REBOUND, %
PLASTICIZER - PARTS BY WEIGHT
X = DIBUTYL PHTHALATE
O = TRIBUTOXYETHYL PHOSPHATE
Δ = CUMAR P-25
□ = OCTADECENE NITRILE
● = DIBUTYL SEBACATE

FIGURE 4. EFFECT OF VARIOUS PLASTICIZERS ON RESILIENCE VULCANIZED NITRILE RUBBER

FIG. 4.—Effect of various plasticizers on resilience of vulcanized nitrile rubber.

plastic compositions, but which has been largely overlooked in the synthetic rubber literature. This is the matter of efficiency which has been discussed in excellent fashion by Boyer and Spencer[6]. Both compatibility and efficiency are indicated by their treatment to be ultimate functions of temperature coefficient of viscosity.

MECHANISM OF PLASTICIZER ACTION

Considerable attention has been devoted in the technical literature to problems associated with the mechanism of plasticizer action, but relatively little attention has been devoted to the class of polymers being considered here, probably because of the complexities previously noted.

Numerous workers in the field of plasticization have attempted to group together all plasticizers for thermoplastics into two broad classes—solvents and nonsolvents. This classification has been useful, but it is obviously inapplicable directly to the system of vulcanized rubbers, simply because there are few solvents for these materials.

Jones and Chadwick[5] have attempted to relate the behavior of typical plasticizers in a vulcanized butadiene-acrylonitrile rubber to the viscosities of the plasticizers. The data presented are limited, and it is believed that further study of this particular factor would show that the indicated simple relation is not general.

Zhurkov and Lerman[6] reported data for combinations of solvents with butadiene-acrylonitrile polymers; these tended to support the senior author's previous hypothesis that all plasticizers (or solvents) are equivalent on a molar basis. Boyer and Spencer[7] have stated their belief that Zhurkov and Lerman's work was based on too few observations. Furthermore, it is extremely doubtful that these generalizations could be extended to the vulcanized state.

Methods of studying the entire polymer-plasticizer system employed by others for determination of the fundamental characteristics of such systems cannot be applied in unmodified form to this system, for reasons given earlier. This would be especially true in the case of dilution ratio measurements of the type employed by Doolittle[8] or even the swelling measurements used by Doty and Zable[9] to determine the μ values (polymer-plasticizer interaction constant) for a series of polyvinyl chloride plasticizers. Direct swelling measurements of vulcanized polymer in plasticizer are possible, as shown by Jones and Chadwick[5], but calibration of the polymer itself is difficult unless suitable solvents are available for osmotic pressure measurements of polymer solutions. However, it is possible to secure an evaluation of the system by indirect means[10].

Swelling results have been reported by Jones and Chadwick[5] for vulcanized Hycar OR-15, a typical butadiene-acrylonitrile rubber. In a series of *n*-alkyl phthalates, the swelling decreased regularly as the length of the alkyl chain increased, until a minimum was reached at the *n*-hexyl derivative, after which the swelling again increased. The parallel with the μ value data reported by Doty and Zable[9] for polyvinyl chloride and with viscosity measurements on the same polymer reported by Frith[11] is strong indication that a common effect must be occurring. The similarity of these effects is illustrated in Figure 5.

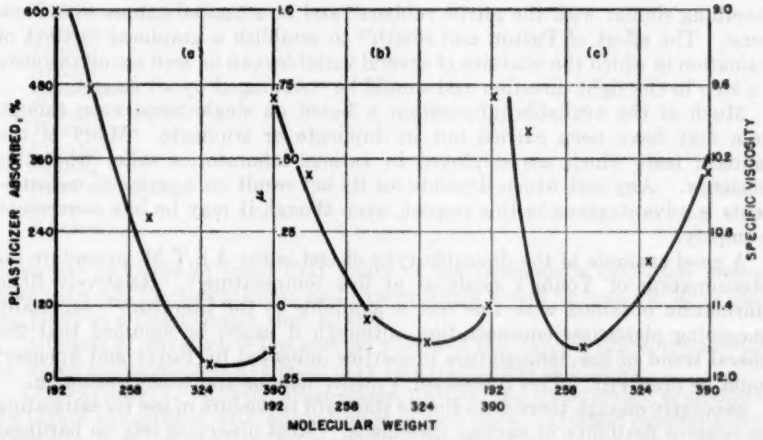

FIG. 5.—Effect of increasing chain length of *n*-alkyl phthalates on (a) plasticizer absorbed by a vulcanized nitrile rubber; (b) polymer-plasticizer interaction constant for polyvinyl chloride; (c) viscosity of polyvinyl chloride solution in plasticizer-solvent blends.

In connection with swelling measurements, the means by which the plasticizer enters the polymer molecule is important in determining the physical character of the resulting product. Table I shows data to illustrate this point.

TABLE I

EFFECT OF OIL IMMERSION ON PHYSICAL CHARACTERISTICS OF NITRILE-TYPE SYNTHETIC RUBBER

	Tensile strength (lb. per sq. in.)	100% stress (lb. per sq. in.)	Elongation (%)
Control (calculated on original dimensions)	2100	1350	200
Control (calculated on final dimensions)	1840	1180	200
Plasticized stock (40 parts plasticizer giving no volume change)	1850	300	360

MATERIALS EMPLOYED AS PLASTICIZERS

Available information.—The literature of plasticizers for the polar synthetic rubbers is extensive, but much of it is of relatively little value to those seeking to determine general relationships. Patents in this field are numerous, and there are several extensive plasticizer studies in the trade literature[12].

Several points become evident when an attempt is made to study the information available. Several screening-type studies have limited themselves to comparative evaluations of a series of plasticizers in a single concentration, with a standard recipe. Such a procedure is of value in eliminating materials which are incompatible, highly volatile, or otherwise objectionable, and in establishing the relative degree of efficiency. Its use in arriving at broad, general conclusions concerning relative effectiveness of widely diversified types of materials is hardly justified, however. It is the author's belief that all materials of definite interest should be evaluated over the entire useful range, and should be compared with one another on the basis of efficiency—for example, other properties can be compared to compositions of the same flexibility or hardness. This practice has been followed in the case of vinyl chloride plastics[13], and it is encouraging to note that an effort has been made to do something similar with the nitrile rubbers[14] and to a limited extent with Neoprene. The effort of Patton and Smith[15] to establish a graphical method of evaluation in which the relations of several variables can be seen simultaneously is a step in the right direction and should be encouraged by all means.

Much of the available information is based on single tests, even though these may have been carried out in duplicate or triplicate. Many of the standard tests which are employed in various laboratories suffer from this deficiency. Any test which depends for its net result on a series of measurements is advantageous in this respect, even though it may be less convenient to employ.

A good example of the desirable type of test is the A.S.T.M. procedure for determination of Young's modulus at low temperature[16]. Relatively little information obtained with this test is available in the literature[17], especially concerning plasticizer concentration, although it might be assumed that the general trend of low temperature properties indicated by Boyer and Spencer[6] would be observed. This procedure is rather tedious and time-consuming.

Strangely enough there is no simple standard procedure in use for estimating the relative flexibility of various specimens. Most observers rely on hardness (which is not an accurate measurement with standard durometers) and simple stress determinations at a predetermined elongation, such as 200 per cent.

It is impossible to estimate small differences by either of these methods, and extrapolation of results with a single plasticizer concentration to those at some other concentration might lead to large errors.

Examination of available information reveals that certain chemical types of materials have been employed as plasticizers for this class of synthetic rubbers. A few general statements may be made concerning their effects, although many of the data are too limited to permit more than tentative conclusions, and many others have been obtained with procedures having large experimental errors, so small differences lose their significance.

The general groups of materials employed may be classified as in Table II.

TABLE II

TYPES OF MATERIALS EMPLOYED AS PLASTICIZERS FOR POLAR SYNTHETIC RUBBERS

A. Hydrocarbons
   - Coal tar distillates (chiefly aromatic hydrocarbons)
   - Asphaltic fluxes
   - Unsaturated hydrocarbons
   - Polybutenes
   - Cyclized or isomerized rubbers
   - Resinous diolefin-styrene copolymers
   - Terpene resins

B. Resins and polymers (not listed in A)
   - Factice
   - Vinyl resins
   - Phenolic resins
   - Alkyd resins
   - Rosin and its derivatives
   - Coumarone-indene resins

C. Esters
   - Esters of dibasic acids (phthalates, adipates, sebacates, succinates, maleates, pelargonates, carbonates)
   - Esters of monobasic acids (benzoates, ricinoleates, stearates, oleates)
   - Esters of dihydric alcohols (triethylene glycol and other polyethylene glycol derivatives)
   - Esters of tribasic acids (phosphates, citrates, aconitates)
   - Miscellaneous esters

D. Miscellaneous chemical types
   - Nitriles
   - Ethers
   - Amides
   - Carbamates
   - Halogen compounds
   - Thiophenols
   - Phenols
   - Sulfides
   - Nitro compounds
   - Amines
   - Ketones

It should be borne in mind that many of the compounds employed possess more than one functional group and consequently would be found in more than one place in a classification such as this.

Analysis of literature.—The specific effects of the various types of materials for which information is available may be summarized as follows:

COMPATIBILITY.—Ethers, ether-esters, nitriles, and unsaturated compounds are highly compatible with all polymers of this class. Limited compatibility, depending both on the specific plasticizer structure involved and on the particular polymer, is shown by saturated hydrocarbons, compounds possessing free hydroxy groups, and by esters containing hydrocarbon chains of greater

than 8 to 10 carbon atoms in length. Aromatic materials are in general more compatible than the analogous aliphatic structures.

Efficiency.—Materials of low molecular weight and especially those of low viscosity are highly efficient. Poor plasticizing efficiency is shown by materials of high molecular weight, especially when this factor is coupled with high viscosity. Resins are almost always inefficient. Those materials which possess limited compatibility are usually inefficient within their compatible range.

Effect on Processing Characteristics.—Most plasticizers assist processing in some fashion. The most outstanding include certain amides, certain carbamates, many resins, some esters, some aromatic hydrocarbons, certain phenols, many amines, and numerous sulfur compounds.

Effect on Cure.—This effect is difficult to evaluate, inasmuch as the particular curing recipe involved determine the specific results. Some amines are known to accelerate curing and retarding effects have been reported for many resins (especially coumarone-indene resins), unsaturated compounds, acidic materials, phenols, and some of the esters of longer chain alcohols.

Permanence.—Polymeric and resinous materials and various processed natural oils are the most permanent, possibly because of their low mobility. The least permanent materials are those which combine high vapor pressure, low viscosity, and high diffusion rate in the polymer. Materials of low compatibility are usually nonpermanent, provided they possess sufficient mobility to migrate to the surface and sufficient vapor pressure to evaporate at that point. Rate of diffusion in the polymeric composition is an important property, but unfortunately quantitative data are lacking.

Aging.—It is almost impossible to generalize concerning the effects of plasticizers on the aging of rubber compositions. A few have definite inhibitory effects on oxidation; some amines and phenols are outstanding in this respect.

Swelling in Hydrocarbon Fluids.—Swelling of the rubber composition in hydrocarbon fluids is increased by the presence of materials of high-viscosity, which presumably cannot be extracted readily by the fluids. Resins and natural oils are outstanding examples of this class. Swelling is decreased in some instances by the presence of materials of low viscosity and high degree of efficiency, including certain nitriles, esters such as dibutyl sebacate and diisobutyl adipate, and certain coal tar distillates; these materials presumably are extracted by the fluid in question. Typical data illustrating these effects are shown in Table III.

Table III

Variable Effects Produced by Plasticizer on Swelling of Nitrile-Type Synthetic Rubber in Hydrocarbon

Plasticizer (50 parts per 100 polymer)	Volume swelling in hexane (%)
None (control)	6.1
Castor oil	12.5
Dibenzyl ether	−17.4
Dibutyl sebacate	−10.8
Diisobutyl adipate	−12.5
Asphalt	12.0
Brown factice	12.5
Light process oil	−10.8
Coumarone-indene resin	14.1
Selected alkyd resin	17.4

WATER RESISTANCE.—Although many plasticizers are relatively insoluble in water, practically all have a deleterious effect on the water resistance of the vulcanized rubber composition. The worst in this respect are those which are water sensitive themselves, such as those containing ether or hydroxyl groups. An exception to this general effect has been noted in the case of Neoprene[18].

EFFECT ON STRESS-STRAIN PROPERTIES.—A few plasticizers show reinforcing effects in the rubber compositions. These are chiefly resinous materials which function as processing aids, and a part of their effect may be simply that of facilitating the fabrication of a more homogeneous composition. A few materials exhibit a weakening effect on the rubber; examples are acidic materials, halogen compounds, and materials of low compatibility.

EFFECT ON RESILIENCE.—Those materials which have the most outstanding effects in improving resilience of the rubber composition are chiefly low-viscosity liquids, including some esters and ethers and a few nitro compounds.

LOW-TEMPERATURE FLEXIBILITY.—The most outstanding materials in improving this characteristic are those of low molecular weight and low viscosity, including especially some ethers, nitriles, and esters containing relatively short hydrocarbon chains. Poor low-temperature flexibility is imparted by cyclic materials, many resins, halogenated compounds, and phenols.

There are many other properties of interest and importance, but the available information is both limited and confusing. It can safely be stated that there is room in this field for extensive additional work. Many of the principles and general observations are similar to those of the plasticized thermoplastics, and any advances in general knowledge will assist in elucidating some of the puzzling problems in the field of plasticized polar synthetic rubbers.

SUMMARY

Natural and synthetic rubbers may be grouped in two broad classes—polar and nonpolar. Dipole linkages are involved in the plasticization of the polar group; hence they possess certain resemblances to the polar thermoplastics in this respect. Plasticizers are employed with such polymers for two general purposes: increasing plasticity of the uncured rubber; and increasing flexibility or corresponding effects in the cured material. Plasticization of the polar rubbers is a complex problem because of structural variations inherent in diene polymers and copolymers; the vulcanization process; and effects of other additives—for example, carbon black. Available data are extremely confusing because of these factors and the fact that much of the information reported is meager. Many of the materials which have been employed may be grouped into a few broad chemical classes. The effects of these vary widely among a given class because of structural variations and differences in physical properties. It is possible to generalize concerning a few types of effects, but more and better data are required before an adequate picture of the plasticization of the polar synthetic rubbers will be available.

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ROLE OF ADSORPTION IN REINFORCEMENT OF GR-S *

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Early tests showed that extra-light calcined magnesia substantially improved reinforcement of GR-S when zinc oxide or other mineral pigments were compounded in it[1]. Furthermore, improved reinforcement was realized only with some of the extra-light calcined (ELC) magnesia products on the market; the majority of these materials and the heavier types of magnesia were ineffective. This observation suggested that the highly adsorptive surface of this pigment was responsible for the improved properties and that certain undesirable short-chain components were removed by adsorption when GR-S was compounded with a selected grade of ELC magnesia. Consequently, the effect of removing the short-chain and partially polymerized materials from the GR-S by solvent extraction was tried. Jones[1] reported that a high degree of reinforcement could be attained by pigmentation with zinc oxide or other noncarbon fillers if GR-S was first extracted with acetone. Since that time the compounding evidence with a number of low-acid GR-S type polymers, which are low in acetone-extractable materials, made available by the Office of Rubber Reserve, further supported these claims. The influence of adsorption in the reinforcement of GR-S was recognized by Goldfinger[2], and some of his observations have been confirmed. Since the preparation of this paper, Baker and Walker[3] have reported the adsorption of GR-S cements on carbon black in conjunction with a project for the Office of Rubber Reserve during the war period.

Recent experiments with light-calcined products other than magnesia are described here. The investigation shows that adsorption plays a part in the reinforcement of GR-S, not only with mineral pigments but also with some of the carbon blacks. The information presented does not account adequately for the overall reinforcement of the pigments in question, but merely offers evidence suggestive of the manner in which the forces of adsorption influence reinforcement with these pigments. For example, the strengthening effect of as little as 5 parts of ELC magnesia to GR-S indicates that this pigment has some specific influence other than that associated with adsorption.

COMPOUNDING TESTS

As an illustration, Table I gives the stress-strain and tear measurements on a number of pigments in GR-S. Tensile and elongation values are charted in Figure 1. Attention is called to the exceptional reinforcement of the surface-active zinc oxide ZnL-1 and aluminum oxide S-1-A prepared by light calcination of basic zinc carbonate and aluminum hydrate [$Al_2O_3 \cdot 3H_2O$], respectively. The stocks pigmented with ELC magnesia and with easy-processing (EPC)

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TABLE I

EFFECT OF PIGMENTS ON PROPERTIES OF GR-S[a]

Pigment	Parts by wt.[b]	Optimum cure at 144.7° C (min.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Load (lbs. per sq. in.) for elongation of			Permanent set at break[c] (%)	Shore hardness	Tear resistance[d] (lbs. per sq. in.)	
					300%	400%	500%			Room temp.	100° C
Whiting	48.2	30	280	375	240	...	...	0.06	45	41	69
Calcium silicate	41.1	45	1270	735	340	510	680	0.19	46	79	40
Kadox-15 zinc oxide	100.0	30	935	605	285	405	570	0.11	43	56	25
Wet-process ZnO ZnL-1	94.6	45	1670	620	580	855	1090	0.60	50	101	64
		90	1715	540	685	990	1485	0.42	55	89	59
Basic zinc carbonate	67.6	45	685	490	405	565	...	0.10	49	60	32
Aluminum hydrate ($Al_2O_3 \cdot 3H_2O$)	41.9	45	815	470	345	560	...	0.09	48	47	22
Aluminum oxide S-1-A	43.0	90	1420	610	345	515	770	0.23	46	74	57
ELC magnesia	57.1	30	2235	570	900	1215	1685	0.77	50	99	86
		90	2550	540	1100	1570	2235	0.56	55	96	54
MPC black	31.2	60	2340	580	635	1110	1620	0.08	47	121	15
Medium-thermal (MT) black	31.2	60	485	825	120	200	285	0.14	34	61	24
EPC black	31.2	60	2260	575	790	1270	1860	0.11	49	112	58

[a] GR-S 100, sulfur 3.5, 2-mercaptobenzothiazole 2, high-melting coumarone-indene resin 7.5, zinc oxide 5 parts, pigment variable.
[b] This loading corresponds to 16.6 volumes of pigment per 100 volumes of GR-S.
[c] Determined by butting the broken tensile pieces together and measuring the set after 3 minutes.
[d] A.S.T.M. tear test D 624–44.

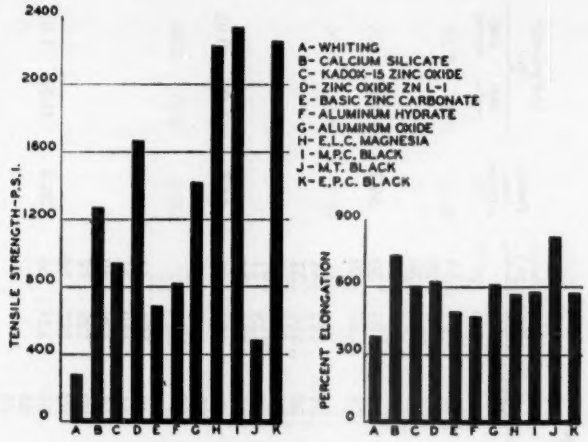


FIG. 1.—Effect of various pigments on tensile strength and elongation of GR-S.

and medium-processing (MPC) channel blacks also had outstanding stress-strain properties. The tensile properties of the other pigments follow in an order that might be expected from their surface areas and activities. In GR-S compounding, the necessity of adapting the formula to the pigment is generally recognized. A compromise formula was used so that all the pigments could be compared in a single recipe, and it is probable that no one of the pigments is shown at its best.

A more detailed picture of the adsorption mechanism is revealed by a series of GR-S compounds pigmented with basic zinc carbonate. The carbonate

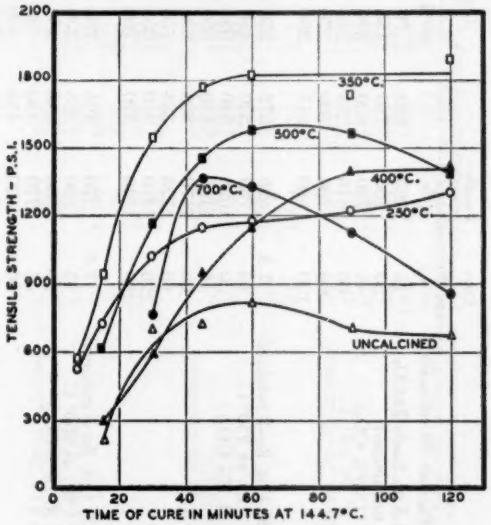


FIG. 2.—Tensile strength of GR-S pigmented with basic zinc carbonate.

TABLE II

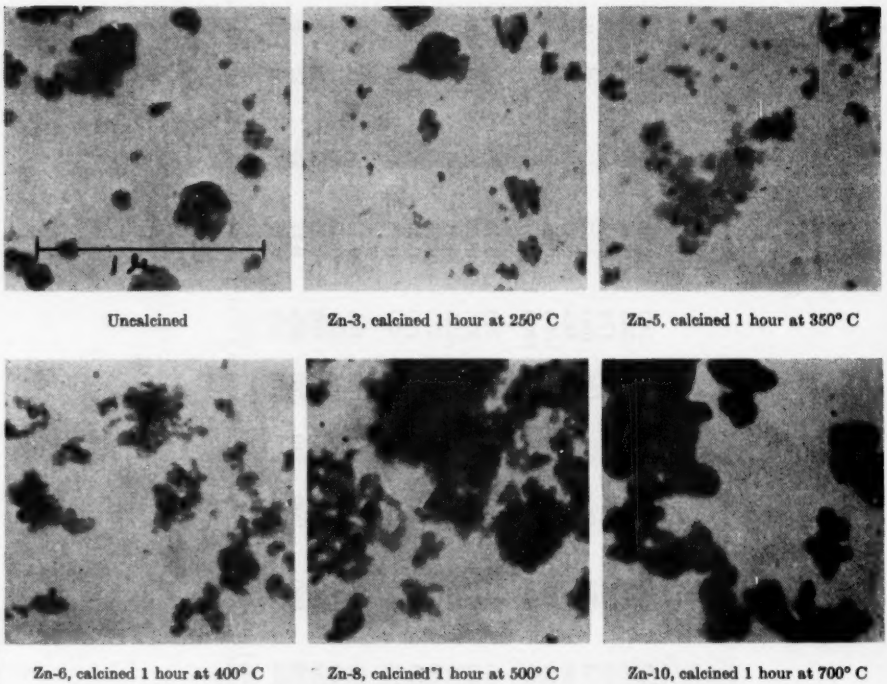
EFFECT OF BASIC ZINC CARBONATE IN GR-S[a]

Pigment (20 volumes)	Cure at 144.7° C (min.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Load (lbs. per sq. in.) for elongation of				Permanent set at break (%)	Shore hardness	Tear resistance (lbs. per in.)		Pendulum, rebound (%)	Cut growth[b] (in.)	
				200%	300%	400%	500%			Room temp.	100° C		1000 cycles	3000 cycles
81.5 pt. basic $ZnCO_3$ uncalcined (15.0% CO_2)	15	205	820	70	105	105	140	0.52	30	36	13			
	30	700	760	155	235	270	350	0.30	45	65	26			
	45	720	620	240	320	400	520	0.19	50	66	30			
	60	815	595	285	365	450	655	0.19	50	60	27			
	90	700	500	270	350	505	700	0.15	51	63	30	55.7	0.57	...
	120	680	515	265	340	450	640	0.14	52	65	30			
120.4 pt. Zn-3 calcined 1 hr. at 250° C. (1.1% CO_2)	7.5	525	375	350	455	...	...	0.20	54	112	44			
	15	730	320	450	695	...	...	0.19	56	116	57			
	30	1025	340	625	880	...	...	0.19	59	122	59			
	45	1150	340	650	940	...	...	0.19	60	128	71			
	60	1170	360	695	955	...	...	0.18	61	130	52			
	90	1225	335	755	1120	...	...	0.16	62	124	61	53.1	0.29	0.95
	120	1310	340	655	1115	...	...	0.13	62					
	180	1240	320	700	1200	...	...	0.11	62					
120.4 pt. Zn-5 calcined 1 hr. at 350° C. (0.76% CO_2)	7.5	570	495	235	370	470	...	0.33	49	124	44			
	15	940	495	350	520	765	...	0.33	54	119	41			
	30	1540	485	580	855	1195	...	0.45	58	128	42			
	45	1770	480	635	955	1350	...	0.44	60	129	97			
	60	1820	455	690	1020	1455	...	0.44	62	132	58			
	90	1740	415	730	1110	1670	...	0.32	64	124	58	53.1	0.49	1.0
	120	1900	395	855	1320	...	...	0.25	65					
	180	2060	400	815	1360	2060	...	0.25	65					

120.4 pt. Zn-6 calcined	15	290	830	70	110	145	180	0.62	31	73	8		
1 hr. at 400° C.	30	590	765	110	150	260	335	0.41	39	87	13		
(0.48% CO_2)	45	955	735	145	220	330	475	0.38	41	101	18		
	60	1150	670	185	295	445	665	0.32	45	96	21		
	90	1400	645	225	340	565	865	0.33	47	93	55	55.4	0.09 0.32
	120	1410	575	260	445	705	1070	0.26	50	95	57		
	180	1730	560	330	575	865	1400	0.27	50				
120.4 pt. Zn-8 calcined	15	625	955	110	145	185	220	0.45	33	105	7		
at 500° C.	30	1160	875	110	185	260	375	0.34	39	104	26		
	45	1455	825	150	225	335	485	0.31	41	122	29		
	60	1580	755	190	270	385	575	0.28	45	120	35		
	90	1570	695	185	300	450	710	0.24	47	110	24	55.7	0.18 0.46
	120	1400	620	225	340	530	830	0.18	49	103	26		
120.4 pt. Zn-10 calcined	30	775	1065	115	115	155	195	0.42	34	142	31		
1 hr. at 700° C.	45	1370	1015	120	155	195	235	0.37	39	111	45		
	60	1330	780	160	200	285	405	0.22	44	85	39		
	90	1130	660	200	240	360	525	0.17	49	71	16	53.7	0.32 0.74
	120	865	570	205	290	370	575	0.15	50	61	21		

[a] GR-S 100, sulfur 3, benzothiazyl disulfide 1, stearic acid 1.5 parts.
[b] Resistance to cut growth determined on DeMattia flexometer in accordance with A.S.T.M. Tentative Method D 813–44T at 70° C.

was calcined over a range of temperatures from 250° to 700° C, and the products were compounded in 20-volume loadings in a GR-S stock. The reinforcing properties developed are shown in Table II and Figure 2. The uncalcined basic zinc carbonate developed relatively low physical properties. However, calcination at 250° to 350° C resulted in a sharp increase in ultimate tensile strength and tear resistance at both room temperature and 100° C. When the calcination temperature was increased to 400° C and higher, there was a reduction in the tensile properties to a somewhat lower range. The electron micrographs of Figure 3 demonstrate the transition in the surface characteristics



Uncalcined | Zn-3, calcined 1 hour at 250° C | Zn-5, calcined 1 hour at 350° C

Zn-6, calcined 1 hour at 400° C | Zn-8, calcined 1 hour at 500° C | Zn-10, calcined 1 hour at 700° C

FIG. 3.—Electron micrographs showing calcination of basic zinc carbonate (×33,000).

and particle size of the basic zinc carbonate. In the range 250° to 400° C, it partially decomposes, and the surface area greatly increases as the carbon dioxide and water molecules are driven from the pigment. This change is believed to take place without appreciably altering the original basic zinc carbonate crystal structure but leaving the particles with a high degree of surface activity due to porosity and unsatisfied surface forces. The samples calcined in the range 300° to 400° C develop the maximum reinforcement in GR-S (Table II). Furthermore, these samples retard the cure, presumably owing to the partial adsorption of curatives by the surface-active pigments. As the temperature of calcination is increased, the porosity of the particles is destroyed, the crystalline configuration is changed to normal zinc oxide, and there is a distinct growth in particle size. The loss in surface activity along

with the growth in particle size of the pigment is reflected in a reduction in the reinforcing properties of the more highly calcined products.

MAGNESIA-PIGMENTED GR-S CEMENT

Adsorption appears to play a dual role in the compounding experiments. First, the adsorption of curatives from the GR-S results in a variation in state of cure of the rubber matrix and an effect on the strength or apparent reinforcement of the system. Second, there is an adsorption effect which involves only the physics of the reinforcing process. In this respect adsorption may act to increase the adhesion between polymer and pigment possibly, as Goldfinger suggested[2], by preferential adsorption of certain molecular weight fractions of butadiene-styrene copolymer. The authors could think of no clear-cut way of distinguishing between these chemical and physical effects by further compounding experiments in GR-S. Tests are available to identify the state of cure of natural rubber compounds with reasonable accuracy, but this is not true of GR-S. Goldfinger[2] studied the adsorption by carbon black from GR-S cements. His technique seemed specially adapted to the study of mineral pigments. It should be possible to determine the nature of the material adsorbed and of the remaining polymer by chemical analysis and physical testing.

A preliminary experiment was made with 60 grams of GR-S and 15 grams of ELC magnesia. The GR-S was dissolved in 3 liters of toluene; after the cement was completely homogeneous, the ELC magnesia was stirred in and allowed to stand in contact with the cement for one week. The cement was centrifuged and analyzed; an unpigmented control cement was also analyzed. The ash content of the polymer recovered from the clear cement was 0.58 per cent and that from the pigmented cement, 0.36 per cent. This demonstrates that the magnesia is effectively removed in the centrifuging operation. Analysis of the material removed from the cement showed 21 per cent organic substances and the balance magnesia. This is equivalent to adsorption of 5.25 per cent of the weight of the original GR-S on the pigment. The fact

TABLE III

STRESS-STRAIN DATA ON POLYMERS RECOVERED FROM CLEAR AND PIGMENTED GR-S[a] CEMENTS

Cure at 144.7° C (min.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Load (lbs. per sq. in.) for elongation of				Permanent set at break (%)
			200%	300%	400%	500%	
Polymer recovered from GR-S-toluene control cement							
7.5	990	715	150	245	295	445	0.17
15	1000	570	190	285	380	620	0.16
30	770	440	240	385	530	...	0.05
45	610	420	255	355	505	...	0.04
60	760	440	240	380	570	...	0.04
90	675	380	335	435	...	...	0.03
Polymer recovered from pigmented GR-S-toluene cement							
30	1650	835	200	300	400	500	0.43
45	1665	785	240	335	430	570	0.42
60	2145	770	245	340	440	635	0.45
90	1645	670	290	435	530	770	0.29
120	1665	635	380	475	620	810	0.25

[a] Polymer 100, sulfur 2.5, 2MT 0.75, 808 0.15, zinc oxide 100 parts.

that approximately 80 per cent of the fatty acid adsorbed on the magnesia was in the form of a soap indicates that the phenomenon is essentially chemisorption.

The polymers recovered from the clear and the pigmented cements had stress-strain properties as noted in Table III. It is evident that the polymer recovered from the pigmented cement is definitely stronger than the control, since it has higher tensile strength and elongation and equal modulus, but cures more slowly.

EFFECT OF VARIOUS PIGMENTS ON CEMENTS

Twelve pigments were selected on the basis of accumulated experience and the information in Table I. Whiting and aluminum hydrate were thought to have little surface activity; basic zinc carbonate and Kadox zinc oxide were considered intermediate; calcium silicate, wet-process zinc oxide, aluminum oxide, and magnesia were thought to have a high degree of surface activity. Three rubber-grade carbon blacks and one adsorbent carbon were included.

A single lot of GR-S, designated X-224, was used in all experiments. It was masticated 30 minutes on a cold mill, and 120 grams was dissolved in 6 liters of purified toluene in two 3-liter brown glass bottles. After the cements were homogeneous, 30 grams of pigment was added, and the bottles were rotated for 72 hours. The pigmented cements were allowed to stand at room temperature for at least one week. The cements were clarified by passage through an air-driven Sharples laboratory centrifuge. With most of the pigments, two passes through the centrifuge gave complete clarification, but twelve passes were necessary for some of the carbon black cements.

The clarified cements were analyzed to determine the amount of pigment left in the cement after centrifuging. The sedimented pigment was collected on a celluloid liner inserted in the centrifuge bowl. Adsorbed GR-S or other organic material in the inorganic pigments was determined by ashing the sample at 650° to 800° C. A sample of the original pigment was placed in the furnace next to the sample containing adsorbed GR-S. This blank was necessary, since many of the pigments lost weight when heated at the temperature required to burn off the organic substances. Free carbon was determined in the carbon black samples recovered in the centrifuge by A.S.T.M. Method D 297–43T. The GR-S in the clarified cements was recovered by evaporation of solvent. As a control, an unpigmented cement was carried through the centrifuging and solvent evaporation steps.

The recovered GR-S was tested in the following formula, unless otherwise noted:

Polymer	100 parts
Sulfur	2.5
2MT	0.75
808	0.15
Zinc oxide	100

Stress-strain properties were determined over a range of cures at 144.7° C. Because of the low strength of GR-S gum stocks, it seemed advisable to test the recovered GR-S in a pigmented compound.

Table IV shows the results. The stress-strain data in Tables III and IV were obtained by the same procedure, *i.e.*, the polymers recovered from the adsorption experiments were mixed in an identical formula, with zinc oxide as the sole pigment. In contrast, Table I shows the results of tests in which the several pigments were mixed directly into the polymer. The stress-strain

TABLE IV

PHYSICAL PROPERTIES OF RECOVERED POLYMER AND ADSORPTION BY PIGMENTS IN GR-S-TOLUENE CEMENTS

Pigment	Optimum cure at 144.7° C (min.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus (lbs. per sq. in.) for elongation of		Permanent set (%)	Shore hardness	Soln. viscosity of recovered polymer (sec.)	% of original GR-S removed by adsorption	% Ash in clarified cements	pH
				200%	400%						
Whiting	40	1040	450	245	595	0.10	50	153.4	1.2	0.23	9.1
Calcium silicate	45	1600	690	200	500	0.23	44	163.5	3.8	0.25	9.1
Kadox-15 ZnO	25	1230	570	245	545	0.06	47	155	2.9	0.58	7.6
Basic zinc carbonate	45	1250	650	200	450	0.13	46	157.25	3.4	None	8.9
Wet-process ZnO ZnL-1	45	1480	750	200	345	0.20	44	159	4.2	0.26	9.7
Aluminum hydrate	40	1100	480	250	650	0.10	51	152.5	0.6	0.10	10.2
Aluminum oxide S-1	30	1680	790	200	345	0.33	42	159.5	3.7	0.08	9.9
ELC magnesia	60	1770	720	255	555	0.39	46	163.5	3.9	0.38	11.2
MPC black	15	1185	580	190	525	0.17	47	154.2	4.5	0.18	5.5
MT black	15	1100	580	195	440	0.12	46	158.1	2.6	0.09	9.0
EPC black	15	1335	600	200	395	0.18	47	160.5	4.5	0.10	4.8
Activated carbon	20	1040	520	200	495	0.14	48	154.6	4.3	0.04	8.2
Control	30	950	450	300	750	0.09	50	148	...	0.38	...
X-224 GR-S[a]	30	960	500	255	555	0.09	49	...	...	0.31[a]	...

[a] Not made into a cement.

results in Table IV fail to show as sharp a distinction between the recovered polymers and control as was obtained in the preliminary experiment (Table III). There are definite trends in the data for the mineral pigments and for the rubber-grade carbon blacks, but a number of factors indicate it is best to consider them separately. In the following table the mineral pigments are listed in order of decreasing adsorption, tensile strength, and solution viscosity:

Adsorption		Tensile Strength		Viscosity	
Wet-process ZnO	4.2	Magnesia	1770	Magnesia	163.5
Magnesia	3.9	Al oxide	1680	Ca silicate	163.5
Ca silicate	3.8	Ca silicate	1600	Al oxide	159.5
Al oxide	3.7	Wet-process ZnO	1480	Wet-process ZnO	159.0
Basic $ZnCO_3$	3.4	Basic $ZnCO_3$	1250	Basic $ZnCO_3$	157.2
Kadox-15	2.9	Kadox-15	1230	Kadox-15	155.0
Whiting	1.2	Al hydrate	1100	Whiting	153.4
Al hydrate	0.6	Whiting	1040	Al hydrate	152.5
		Control	950	Control	148.0

The polymers having the highest tensile strength and solution viscosity were recovered from the cements containing the most highly adsorbing pigments. The lower tensile, low viscosity polymers were recovered from cements containing pigments of weak adsorbing power. The alignment is not perfect, and it would be unwise to conclude that the difference in tensile strength between polymers recovered from Kadox-15 and ELC magnesia was due to a difference in polymer adsorption. With both these pigments chemical reaction occurs at the particle surface and this affects the curing process of the recovered polymers by leaving them deficient in some of the curative ingredients. On the other hand, the light calcination of aluminum hydrate converts it from a very weak adsorbent to one of the strongest adsorbents, with a corresponding change from a weak to a strong recovered polymer. This could be a true physical effect since the rate of curing of the recovered polymers is nearly the same, and the aluminum hydrate and oxide are relatively inert chemically.

There are some interesting differences in the curing rates of the recovered polymers. Those recovered from the cements pigmented with carbon black are faster curing than the control; that from the magnesia-pigmented cement is definitely slower than the control; those from the calcium silicate, basic zinc carbonate, and wet-process zinc oxide cements appear slightly slower than the control. There is no apparent relation between the rate of curing of the recovered polymers and their ash content or the amount of adsorption from GR-S in the pigmented cements. One would expect some connection if there was strong selective absorption of the acids in GR-S, because removal of these acids by extraction results in a very slow curing rubber. There does not appear to be any fundamental connection between the pH of the pigments and their adsorption. While water slurries of all the noncarbon pigments in Table IV are alkaline, some of the highly adsorbent blacks are acidic. The pH values of the weakest adsorbing pigments, whiting and aluminum hydrate are in the same range as some of the adsorptive pigments.

The modulus and hardness values in Table IV show that, as adsorption from the cements increases, modulus and hardness decrease in the zinc oxide stocks made from the recovered polymers. A similar effect was noted by Goldfinger[4]. This does not appear to be a matter of curing rate since the modulus and hardness of the recovered polymers from which there has been a high degree of adsorption will not attain the values for the control even after

very long curing times. The possibility must be considered that the pigments have removed some material essential for a balanced compound.

ADSORBED FRACTIONS

An analytical study was made of the polymers separated from the GR-S cements after they were in contact with ELC magnesia, calcium silicate, and EPC carbon black, and also of the fractions adsorbed by these pigments. These were considered representative of the several adsorptive pigments investigated. Hereafter the polymer recovered from the GR-S cement will be called *recovered polymer*, and the material adsorbed on the pigment will be designated *adsorbed fraction*. The term polymer is not employed because in most cases the adsorbed fraction is soft and greaselike, owing to the high soap and fatty acid content, and does not resemble a polymer.

In recovering the adsorbed fraction for analysis, the pigments were allowed to stand for several days in a large volume of toluene. The suspension was centrifuged and the adsorbed fraction recovered by evaporation of the toluene. The final traces of organic material were recovered by dissolving the ELC magnesia or calcium silicate in dilute hydrochloric acid and extracting with ether. The organic fraction was combined with that portion removed from the pigment by solution with toluene. The adsorbed fraction was separated from EPC black by repeated washings with large volumes of toluene, as the acid treatment was not effective.

The analytical results (Table V) are most definite for the samples recovered in the magnesia experiment. Fatty acids and soap account for 49.1 per cent of the fraction adsorbed by magnesia. This represents practically all the ETA extractable in the fraction. ETA stands for ethanol-toluene azeotrope, the constant-boiling mixture of 70 parts of ethanol and 30 parts of toluene by

TABLE V

ANALYSIS OF ADSORBED FRACTIONS AND RECOVERED POLYMERS

Adsorptive pigment	Calcium silicate		EPC black		Magnesia		
Analysis (grams)							
GR-S, at start	120		120		120		
Pigment used	30		30		30		
Pigment recovered	31		...		31		
Adsorbed fraction recovered	2.2		2.1		5.6		
Polymer recovered	116		114		107		
	Recovered polymer	Adsorbed fraction	Recovered polymer	Adsorbed fraction	Recovered polymer	Adsorbed fraction	X-224 GR-S control
ETA extractable[a] (%)	5.8	19.3	22.6	48.6	3.7	54.6	7.71
Fatty acid and soap[a] (%)	4.5	13.1	4.9	5.7	2.3	49.1	5.4
Index of refraction[b]	1.532	1.533	...	...	1.534	1.534	1.534
% styrene[c]	20.7	21.9	...	...	23.1	23.1	23.4
% gel before extn.[d]	1.4	...	1.9	...	2.4	...	2.0
Soln. viscosity, sec.[e]	146	...	148	...	149	...	146

[a] Percentages are based on weight of recovered polymer and adsorbed fractions, except for control (ETA = ethanol-toluene azeotrope).
[b] Run on ETA extracted portion at 25° C.
[c] Styrene content calculated from index of refraction.
[d] Insoluble in benzene; based on weight of ETA extracted portion.
[e] Efflux time at 27° C; 0.5% solutions in toluene in a Bingham capillary viscometer; samples not extracted.

volume used in extraction[5]. From refractive index and benzene solubility tests, the remainder has the same styrene and gel content as the original GR-S, and may be presumed to be butadiene-styrene not significantly different from that in the original polymer. The refractive index measurement has been widely used as a control test for determining the styrene content of GR-S[6]. The adsorption by magnesia is strongly selective. The concentration of fatty acid and soap in the adsorbed fraction is almost ten times that in the original GR-S. The analysis of the polymer recovered from the cement agrees with the values for the adsorbate. Except for less fatty acid, soap, and ETA extractable, the recovered polymer shows no significant difference from the original GR-S.

Calcium silicate also adsorbs fatty acid and soap selectively, but not so strongly as does magnesia. Thirteen per cent of the total adsorption by calcium silicate is fatty acid and soap. This represents a concentration of about 2.5 times that in the original polymer. The index of refraction and benzene solubility tests on the samples obtained in the calcium silicate experiments are not very good. Since the determinations on the recovered polymer check those on the material adsorbed on the pigment, it is believed that there is no difference in styrene or gel content between the recovered polymer and adsorbed material. However, both values are at considerable variance with corresponding determinations on the original GR-S.

With carbon black the distribution of fatty acid and soap is the same in the recovered polymer and adsorbed fraction, and equal to the original GR-S. Evidently there is no selective adsorption of fatty acid and soap by the black. The values for the ETA extractable material in the fractions recovered from the carbon black experiment call for some comment. If this value is higher than the control in the adsorbed fraction, it should be lower in the recovered polymer. The polymer recovered from the cement in the carbon black experiment has three times as much ETA extractable as the control, and the fraction adsorbed on the pigment, over six times as much ETA extractable. A satisfactory explanation cannot be offered for this apparent anomaly, which might be due to experimental error.

If the analytical information for magnesia and calcium silicate in GR-S is representative of the behavior of pigments other than carbon black, it is doubtful whether the effect of vulcanization chemistry and reinforcement physics can be clearly segregated. Changes in the effective concentration of fatty acids influence the chemical state of cure, and a large part of the adsorbed material in the case of magnesia and calcium silicate has consisted of the fatty acid in the polymer. It is hoped that a further study of pigment adsorption will serve to differentiate between the chemical reinforcement of the polymer and the physical aspect of the problem dealing with the pigment-to-polymer bond.

SUMMARY

1. The reinforcement of GR-S is influenced to an appreciable extent by the adsorption characteristics of pigments compounded in this polymer.

2. The relation between surface activity and reinforcing properties of a pigment in GR-S is demonstrated in the case of a basic zinc carbonate calcined through a range of temperatures.

3. Twelve pigments were immersed in GR-S cement, and the recovered polymer was evaluated. The mineral pigments, ELC magnesia and calcium

silicate, selectively remove fatty acids and soaps from GR-S cements. The adsorption by EPC black is not selective with respect to fatty acids and soaps. The effects obtained on testing the recovered polymer vary in line with the amount and nature of the adsorption.

4. With ELC magnesia and calcium silicate, the effect of adsorption is predominantly due to the removal of fatty acids and soaps, and this affects the vulcanization chemistry. The process is different with EPC black, but a clear interpretation is not possible on the basis of present experimental data.

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IMPROVED-PROCESSING GR-S BY VARIATIONS IN COMPOUNDING *

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During 1946 considerable work was done in attempting to improve the processibility of GR-S. Among the variations tried were the blending of high-gel high-Mooney-viscosity polymers with polymers of very low Mooney viscosity, the preparation of high-gel polymers by the introduction of divinylbenzene into the polymerization charge, the production of high-gel polymers by means of normal and tertiary thiol modification and additional butadiene in high conversion polymers, and finally the changes in compounding and processing reported here.

GR-S cross-linked by means of 0.5 part of divinylbenzene per 100 parts of monomer was produced as X-285 of the Office of Rubber Reserve series, and was later designated GR-S-60. Previous work on similar polymer (80 per cent gel content and 55–60 Mooney viscosity), alone or blended with regular GR-S in amounts up to about 75 per cent, showed this type of polymer to exhibit less shrinkage and superior extrusion, surface appearance, and general processibility in calendered, extruded, and molded stocks. Blending of the GR-S-60 with GR-S was expected to produce a stock with physical properties that were lacking when GR-S-60 was used alone.

Since divinylbenzene was in short supply, and because it was felt that the degradation of physical properties might severely limit its use, a program was undertaken to cross-bond GR-S by means of sulfur at high processing temperatures. Preliminary work indicated that this procedure yields improved processing which approaches that of GR-S-60, as well as maintains physical properties near those of regular GR-S and far better than those of GR-S-60 alone. The preliminary program was concerned with limited attempts to improve processing. The second phase of the program was confined to the use of sulfur or a sulfur-yielding agent to select the best procedure. The third phase comprised testing various sulfur-yielding agents, thermosetting resins, or other cross-bonding agents by means of the best procedure developed in the second phase of the study.

RECIPE AND MIXING

The following compounding recipe, specified for GR-S, was employed for all tests in this study: polymer, 100 parts; EPC black, 50; zinc oxide, 5; BRT No. 7, 5; sulfur, 2; 2-mercaptobenzothiazole, 1.5. Mill mixing, where used,

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TABLE I

PHYSICAL PROPERTIES OF GR-S-60, GR-S, AND BLENDS OF GR-S-60 WITH GR-S

Polymer	Mooney viscosity: Raw ML-4[c]	Mooney viscosity: Compd. MS-4[d]	Roughness[e]	Mill shrinkage (%)	Mooney scorch (cure) index[f] (min.)	Optimum cure[g] (min.)	Cure at 292° F (min.)	300% modulus[h] (lbs. per sq. in.)	Tensile strength[h] (lbs. per sq. in.)	Elongation[h] (%)	Set[h] (%)	Extrusions. index[i]
Mill-mixed stocks												
GR-S-60[a]	61	72	5	8	36.8	..	30	1480	1870	370	7	16
50/50 GR-S-60/GR-S	52	47	16	16	54.5	66	60	1670	2810	440	8	14.5
30/70 GR-S-60/GR-S	51	40	18	21	53.5	64	60	1590	3130	500	11	13
10/90 GR-S-60/GR-S	49	39	23	29	58.0	68	60	1380	3250	560	14	13.5
GR-S	49	34	44	42	...	48	45	1080	3200	640	..	...
Banbury-mixed stocks (including mastication for 2 min. at 380° F with 0.5 part S and 0.5 part Captax)												
GR-S 60[b]	61	74	9	..	29.5	..	30	....	1870	280	6	10[j]
50/50 GR-S-60/GR-S	52	..	6	15	67	..	60	....	1440	155	1	5[k]
30/70 GR-S-60/GR-S	51	..	7	23	59	..	60	....	1980	235	2	3.5
10/90 GR-S-60/GR-S	49	..	15	29	70	..	60	....	2030	260	2	14.5
GR-S	..	..	10	19	39	..	45	....	2140	250	2	12

[a] Raw GR-S-60 subjected to 5-minute warm-up in Banbury at maximum temperature of 380° F before mixing on mill. Actual time at 380° F, less than 1 minute

[b] GR-S-60 mixed with all materials except zinc oxide, sulfur, and Captax in the Banbury for 5 minutes at a maximum temperature of 380° F. Actual time at 380° F, probably less than 1 minute.

[c] Large rotor; 4 minutes in viscometer at 212° F.

[d] Small rotor; 4 minutes in viscometer at 212° F.

[e] Roughometer or rugosimeter index.

[f] Time at which Mooney (ML-4) viscosity of a sample of test polymer is 30 points higher than lowest reading when tested at platen temperature of 300° F test outlined by Juve[1].

[g] Optimum time of cure was time at which a line, drawn parallel to the straight line connecting the end cure points of the 300% modulus *vs.* time of cure curve, was tangent to the curve obtained by plotting the moduli at 30, 45, 60, 90, and 150 minutes of cure.

[h] Values for modulus, tensile strength, elongation, and set are given for 30-, 45-, 60-, 90-, and 150-minute cures, whichever was closest to optimum cure, as determined by either 300% modulus or Mooney viscosity scorch index (footnotes *f* and *g*).

[i] Uncured compound tubed through a Garvey die on No. ½ Royle extruder and rated as described by Garvey, Whitlock, and Freese[2].

[j] Edge rated as zero (very badly split); porosity, corners, and surface alone made up rating of 10.

[k] Polymer unsuitable for tubing.

was accomplished according to the procedure described in the specifications[3]. Banbury mixing was usually effected by placing polymer with cross-linking agents, if any, in a warm (about 200° F) Banbury, and, after 2 minutes of mastication, adding the black in three equal portions one minute apart. The rotor speed was varied to allow the internal temperature of the Banbury to reach 380° F and remain at that point for a specified time. The zinc oxide and softener were then added to the stock at intervals of one minute. The material was dumped and (after cooling the polymer to about 200° F) mixed with sulfur and 2-mercaptobenzothiazole on a 10 × 20 inch mill. Variations from this method are noted in the discussion of the particular experiments. All testing was in accordance with the regular specification procedure of the Office of Rubber Reserve[3].

The following materials were used in attempts to cross-bond GR-S in this experiment; combinations of one or more of them with GR-S are noted in the discussion: TTDE (trithiodiethylamine), methyl Tuads (tetramethylthiuram disulfide), ethyl Tuads (tetraethylthiuram disulfide), Monex (tetramethylthiuram monosulfide), Selenac (selenium diethyldithiocarbamate), Vandex (elementary selenium), Telloy (elementary tellurium), Butyl Eight (dithiocarbamate mixture), sulfur, thio-β-naphthol, Captax (2-mercaptobenzothiazole), Altax (dibenzothiazoyl disulfide), Sulfasan (bis-ethylthioxanthogen), Dixie (bis-isopropylxanthogen), *tert*-octanethiol Thiofide (2,2′-dithio-bis-benzothiazole), sodium dimethyldithiocarbamate, methyl Zimate or Methasan (zinc dimethyldithiocarbamate), Rosin Amine D, Tetrone-A (dipentamethylenethiuram tetrasulfide), divinylbenzene solution (Dow Chemical Company, monomer Q302.4), Durez resin No. 12687, 7031A, or 11078, Polyac (*p*-dinitrosobenzene with inert filler), GMF (*p*-quinonedioxime), diallyl phthalate prepolymer or monomer, and Amberol No. ST-137 or ST-137X.

For measuring the improvements produced by the various modifying agents, two sets of standards were examined. For judging the Banbury-mixed batches, GR-S-60 was compounded in the Banbury according to the specification recipe[3] at a maximum temperature of 380° F. Blends of GR-S-60 with various amounts of GR-S were also treated with sulfur and Captax at high temperatures during the mixing cycle. In judging the mill-mixed stocks, GR-S-60 pretreated in a Banbury for 5 minutes at a maximum temperature of 380° F and blends of GR-S-60 and GR-S that had received no pretreatment in the Banbury were used.

Table I summarizes data relating to these standards. The divinylbenzene polymer showed extremely good processibility (rated by mill shrinkage, roughness, and extrusion index) when the stock was mill-mixed. Stress-strain qualities, however, were poor. In blends with GR-S, as the quantity of GR-S-60 decreased, ease of processing also decreased, but the stress-strain quality improved. The data show that perhaps a 50/50 or 30/70 GR-S-60/GR-S blend would give almost normal stress-strain properties with a large improvement in processibility over that of GR-S alone.

When mixes of GR-S-60 in the Banbury reached temperatures around 380° F, even for a very short period, both the processibility and stress-strain properties were poor. In fact, a stock containing 30 GR-S-60 and 70 GR-S showed better processibility than could be obtained with larger quantities of GR-S-60. Tensile strength values were still only about 2000 pounds per square inch. Equal or better properties were shown for GR-S alone which had been treated with 0.5 part each of Captax and sulfur as cross-linking agents for a 5-minute period at 380° F during the mixing cycle.

TABLE II

VARIATION IN POINT OF ADDITION OF ZINC OXIDE[a]

Point of addition of zinc oxide	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
100 Parts GR-S, 0.5 TTDE, 0.25 Captax charged initially; Banbury temp. brought to max. of 380° F during mixing, but not held at that temp.									
After 380° F	26	31	..	30	2260	3300	390	7	11
In initial charge	32	31	..	20	2480	2960	340	5	11
100 Parts GR-S, 0.5 TTDE, 1.5 Captax charged initially; Banbury temp. brought to max. of 380° F and held there 5 min.									
After 380° F	5	19	49	60	....	1950	250	2	13
On mill at end of mixing	11	22	85	50	....	1900	260	3	15

[a] Properties are explained in Table I.

TABLE III

VARIATION IN CONCENTRATION OF CAPTAX IN INITIAL BANBURY CHARGE

Captax	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
Mixed for 5 min. in Banbury at 380° F, with initial charge of 100 parts GR-S, 0.5 TTDE, and Captax									
0.25[a]	11	34	42	23	2600	2740	315	3	13
0.50	9	17	76	95	1540	2060	355	7	12
1.0	8	33[b]	82	62	....	2040	265	3	12
1.5	5	19	49	65	....	1980	245	2	13
Mixed for 5 min. in Banbury at 380° F, with initial charge of 100 parts GR-S, 0.5 sulfur, and Captax; 0.5 to 1.0 part of additional Captax added with remainder of sulfur (1.5 parts) on mill									
0.50	18	20	52	60	....	2220	275	3	10
1.5	12	23	82	60	....	2050	240	3	14

[a] 1.25 parts of additional Captax added on mill with sulfur (2 parts) after dumping from Banbury.
[b] Probably in error.

EFFECT OF VARIABLES

Variation in the point of addition of the zinc oxide (Table II) showed that, with TTDE, the best properties were obtained when the oxide was added immediately after the 5-minute mastication at 380° F. This procedure produced slightly better appearance, smoothness, mill shrinkage, and extrusion index values than when the zinc oxide was added at any other time.

Variation of the concentration of Captax (Table III) from 0.25 to 1.5 parts per 100 parts of polymer in the initial charge, using TTDE, resulted in little difference in extrusion indices or in mill shrinkage and roughness values that could be correlated with the variation. One and one-half parts of Captax possibly gave slightly better properties than were obtained with 0.5 part. Tensile strengths in almost all cases varied between 2000 and 2700 pounds per square inch, and elongations between 250 and 350 per cent, apparently depending on the amount of cross-linkage developed during the 5-minute mastication. Similar variations (Table III) when sulfur was used instead of TTDE as a cross-linking agent also indicated that improved properties were obtained when the higher proportion of Captax was added in the initial charge.

The mastication periods for the cross-linking agents and the polymers were varied from 1 to 10 minutes at 380° F. It runs where the cross-linking agents were added initially (Table IV), the data show that a period of 2 minutes or less yielded minimum values for roughness and percentage mill shrinkage of about 17 and 28, respectively. Treatment for 5 minutes at 380° F resulted in values of about 5 and 18, respectively; treatment for a 10-minute period produced values of 4 and 13, respectively. Tensile strengths and elongations decreased as the mixing time at 380° F was increased. Extrusion indices were found to be substantially equal at a rating of about 13 (comparable to that of GR-S at 11 to 13 against a theoretical maximum rating of 16).

Cross-linking agents and sulfur were also added on a mill to control batches which were previously mixed with the other ingredients for 1 to 10 minutes in a Banbury at 380° F (Table IV). The data showed no substantial improvement in processing properties with increased reaction time in the Banbury. Moreover, stress-strain properties decreased only slightly as the breakdown time at 380° F was increased. It was thus concluded that the improvement in processibility obtained when sulfur and Captax were added to the initial Banbury charge was due almost entirely to cross-linking produced by these reagents and was relatively unaffected by hot mastication.

Throughout this work, extremely high moduli were observed. It was believed that perhaps adjustment of the total amount of sulfur in the compounding formula might lower the moduli and perhaps result in tensile strengths and elongations more nearly comparable with those of GR-S. Variation was made between 1.0 and 2.0 parts of sulfur per 100 parts of standard GR-S (Table V). The data show that, as the sulfur content was increased, the tensile strengths also increased appreciably (about 400 pounds per square inch) with a slight decrease in elongation and little change in set when the GR-S was mixed with cross-linking agents at 380° F in the Banbury. Similar comparison on batches in which cross-linking agents were added on a mill after the breakdown period at 380° F indicates little or no change in tensile strength, modulus, or set, but shows an appreciable decrease in elongation.

Variations were also made in the total of Captax concentration in the formula. Data show that probably at least 1 per cent of Captax was necessary to prevent undercuring or excessive time to attain optimum cure (Table VI).

Table IV

Variation of Time of Mastication in Banbury at 380° F

Min. in Banbury at 380° F	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
100 Parts GR-S, 0.5 TTDE, 1.5 Captax in initial Banbury charge									
1[a]	22	37	40	40	2430	2960	350	4	12.5
2	17	28	80	60	1700	2330	360	5	13.5
5	5	18	49	60	....	1950	240	3	13
10	4	13	72	100	....	1440	265	3	13
100 Parts GR-S in initial charge; black added before 380° F was attained; Zn oxide and softener added after 380° F period; 0.5 part TTDE and 1.5 parts Captax added with sulfur on mill after mixing at 380° F									
<1[b]	18	33	..	20	2750	3060	325	5	10.5
2	16	35	58	20	....	2490	260	3	10
5	29	32	47	20	....	2540	270	4	11
10	14	30	44	15	....	2500	240	3	12.5

[a] Only 0.25 part of Captax in initial Banbury charge; additional 1.25 parts added to stock by milling after material was dumped from Banbury.
[b] Zinc oxide and softener added with black before a maximum of 380° F was reached.

Table V

Variation in Total Concentration of Sulfur in Banbury-Mixed GR-S Stocks

Total sulfur	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
100 Parts GR-S, 0.5 TTDE, 1.5 Captax added in initial charge before 5-min. period at 380° F; sulfur added on mill after 380° F period									
1.0	8	19	49	60	....	1630	290	3	...
1.25	10	19	49	60	....	1890	290	3	...
1.50	8	19	49	60	....	2000	280	2	...
1.75	5	18	49	60	....	1950	240	3	13
100 Parts GR-S initial charge; Zn oxide and softener added before 5-min. mixing at 380° F; 0.5 part TTDE and 1.5 parts Captax added on mill with sulfur after mixing at 380° F									
1.0	31	40	35	15	2200	2510	325	5	...
1.25	39	40	35	20	2450	2530	305	5	...
1.50	44	40	35	20	2370	2410	305	5	...
1.75	40	35	35	20	....	2480	270	4	13.5

TABLE VI

VARIATION IN TOTAL CONCENTRATION OF CAPTAX IN BANBURY-MIXED STOCKS

Total Captax	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
(100 Parts of GR-S, 0.5 sulfur, and 0.5 Captax were added in initial charge before 5-min. period at 380° F; 1.75 parts of additional sulfur and additional Captax were added on mill after the 380° F period)									
0.5	9	20	..	80	1430	1870	345	4	..
1.1	15	20	..	60	....	2150	260	2	..
1.6	10	19	..	40	....	2140	250	2	..

TABLE VII

COMPARISON OF STOCKS BANBURY-MIXED FOR 5 MINUTES AT 380° F IN PRESENCE OF EITHER SULFUR OR TTDE

(100 Parts GR-S, Captax and 0.5 part of TTDE or sulfur in initial charge before 5-min. period at 380° F; no additional Captax added on mill)

	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
0.5 Part Captax in initial charge									
TTDE	9	17	76	95	1540	2060	355	7	12
Sulfur	9	20	..	80	1430	1870	345	4	..
1.5 Parts Captax in initial charge									
TTDE	5	18	49	60	....	1950	240	3	13
Sulfur	9	17	60	60	....	2040	295	3	14

In repeated trials, about 1.5 parts of Captax produced curing times of 40 to 50 minutes and slightly higher stress-strain, modulus, and tensile strength values than were obtained with lower concentrations of Captax.

After several batches had been made, the substitution of sulfur for TTDE as the initial cross-linking agent was attempted (Table VII). Little or no difference was apparent between the two batches with Captax acceleration. TTDE is scarcer and much more expensive than sulfur. The latter would, therefore, be recommended for use.

The data for batches made with 0.5 part of sulfur or TTDE and 0.5 to 1.5 parts of Captax as the initial cross-linking agents of GR-S during Banbury treatment at 380° F for a 5-minute period, and mixed by the method described earlier in the paper, show that both processing and physical properties were equal or superior to those obtained with either GR-S-60 or 50/50 GR-S-60/GR-S blends produced under similar conditions (Table I). In addition, the sulfur-Captax-GR-S stocks, mixed at high temperatures in a Banbury, closely approached the processing properties and were superior in stress-strain properties to divinylbenzene polymer mixed at low processing temperatures. The concentration of sulfur and Captax or time of mixing could be varied further to improve processibility or stress-strain values as required for different products. The maximum change would be a slight increase in the regular Banbury mixing cycle now in use. Special polymer would not be required, nor would any unusual or costly compounding ingredients be needed. One Banbury cycle would serve to compound, cross link, and prepare GR-S for the extruders.

OTHER CROSS-LINKING AGENTS

Data obtained by the use of various combinations of other cross-linking agents listed are summarized in Table VIII. The 5-minute mixing cycle previously described was employed. Only those materials that (1) lowered the mill shrinkage or roughness or (2) raised the extrusion index or stress-strain values were considered worthwhile. Especially noteworthy were the following combinations:

0.5 part Captax, 0.5 part methyl Tuads
1.0 part Ambersol (ST-137)
0.25 part Butyl Eight, 0.5 part sulfur, 0.5 part Captax
0.5 part Durez resin 12687, 0.5 part Captax
0.25 part Vandex or Telloy, 1.0 part zinc oxide, 0.5 part sulfur
0.5 part ethyl Tuads
0.25 part thio-β-naphthol, 0.5 part Captax, 0.5 part sulfur
0.5 part Polyac, 0.5 part Captax
0.1 part Polyac
0.25 part thio-β-naphthol, 0.5 part sulfur
0.5 part Monex, 0.5 part Captax
0.5 part Captax
0.5 part Altax

The presence of Captax possibly accounted for part of the improvement in processing noted in some of these mixtures. The use of Butyl Eight and sulfur without Captax yielded increases of approximately 500 pounds per square inch in tensile strength, 10 per cent shrinkage, and 10 points in roughness, and a decrease of about 2 points in extrusion index, compared to the values obtained when Captax was present in the initial mixture. Similar comparisons were

TABLE VIII

DATA FOR EVALUATION OF VARIOUS CROSS-LINKING AGENTS

(All batches mixed in Banbury for 5 minutes at 380° F after addition of black and before addition of zinc oxide and BRT 7; 1.0 part Captax and 1.75 parts sulfur added to each batch on mill prior to curing)

Initial charge to Banbury	Roughness	Mill shrinkage (%)	Viscosity (compd. MS-4)	Mooney scorch (cure) index (min.)	Optimum cure (min.)	300% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Set (%)	Extrusion index
GR-S 100, methyl Tuads 0.5, Captax 0.5	6	19	40	51	..	....	2040	260	4	15.5
GR-S 100, Ambersol (ST-137) 1	4	24	32	121	70	1850	2560	400	11	16
GR-S 100, Butyl Eight 0.25, S 0.5, Captax 0.5	5	16	45	47	..	....	1930	235	3	15.5
GR-S 100, Durez 12687 0.5, Captax 0.5	27	20	42	72.5	..	....	2280	355	6	15
GR-S 100, Vandex 0.25, Zn oxide 1, S 0.5	19	21	53	83	..	....	2150	265	3	14
GR-S 100, Telloy 0.25, Zn oxide 1.0, S 0.5	16	23	36.5	72	..	2010	2430	335	6	12
GR-S 100, ethyl Tuads 0.5	11	24	32	68	..	2350	2700	345	4	12
GR-S 100, thio-β-naphthol 0.25, S 0.5, Captax 0.5	5	18	46	35	..	1770	1770	300	4	15.5
GR-S 100.0, Polyac 0.5, Captax 0.5	18	22	45	72	..	....	2050	265	3	15
GR-S 100, Polyac 1	20	21	51	71	..	1360	1870	310	4	13.5
GR-S 100, TBN 0.25, S 0.5	10	17	46	96.5	..	....	2060	275	3	13.5
GR-S 100, Monex 0.5, Captax 0.5	18	20	35	70	..	....	2460	295	4	15
GR-S 100, Captax 0.5	8	26	36	75	..	2030	2200	310	6	14
GR-S 100, Altax 0.5	8	26	37	80	..	....	2100	260	4	14.5

made with methyl Tuads, thio-β-naphthol, Durez resin 12687, and Polyac. Only in the cases of thio-β-naphthol and of Polyac was there any indication that Captax would not be necessary to intensify the cross-linking, with consequent improvement in processibility over that obtained with either material alone. The use of the foregoing mixtures, approximately in the order listed, gave indications of at least moderate improvement in processibility similar to that obtained with sulfur and Captax. Perhaps any one of these combinations could be developed somewhat further and substituted for the sulfur and Captax.

SUMMARY

The data indicate that treating GR-S for 5 minutes in the Banbury at 380° F in the presence of the combinations of cross-linking agents listed brings about improvement in processing and stress-strain properties, equal or superior to those produced by sulfur and Captax together. In turn, this GR-S polymer, treated with sulfur and Captax, was shown to be superior to GR-S-60 and to GR-S-60/GR-S blends in ratios higher than 30/70, after mastication and compounding of the polymers in a hot Banbury at about 380° F. The properties of the sulfur-Captax cross-linked GR-S closely approached the excellent processibility and excelled the poor stress-strain characteristics of GR-S-60 compounded by milling at normal temperatures.

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CHARACTERISTICS OF REINFORCING FURNACE BLACKS

PROCESSING SHRINKAGE *

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A major technical development in the rubber industry has been the recent introduction of furnace blacks possessing rubber reinforcing properties in the range of channel blacks. The literature on the subject of reinforcing furnace blacks is rapidly expanding[1] to satisfy the need for information on the compounding and rubber properties of these new products.

Types of reinforcing furnace blacks are available which duplicate closely the usual rubber properties observed with channel blacks in vulcanized stocks. However, because of the flexibility of operation and the different types of raw material adaptable to the continuous furnace process, it is also possible to produce grades of reinforcing furnace blacks which differ markedly from channel blacks in rubber properties. The range of rubber stiffness and hardness obtainable with reinforcing grades of furnace blacks is much greater than with channel blacks, and although final approval of a grade of black for a particular application is based on service testing, the useful range of rubber product quality has been broadened by the introduction of new varieties of furnace blacks.

Processing characteristics of carbon blacks may be described as the relative workability factors of rubber stocks in the sequence of operations preceding the completed manufacture of cured rubber articles. In those compounds where carbon black is a substantial component of the stock, the properties of the black would be expected to exert a major influence on processing.

The work reported here is concerned with the effect of carbon black properties on the forming step of semifinished stocks, and includes a study of the processing shrinkage properties of carbon black loaded stocks.

STRUCTURE IN CARBON BLACKS

Whereas the processing characteristics of channel blacks bear a simple relation to particle size and are the basis for their present classification in the rubber industry, the processing properties of furnace blacks cannot be correlated similarly with the same degree of fineness. It has been necessary to introduce the concept of structure to explain such anomalous properties as the low processing shrinkage and the smooth surface appearance of extruded and calendered stocks observed when certain grades of reinforcing furnace blacks are used. Although these effects are particularly noticeable with GR-S, they can be observed to a lesser degree with natural rubber also. In cured vulcanizates structure blacks are characterized by high modulus and hardness, low breaking elongations, and high electrical conductivity.

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No conclusive evidence is available to show whether these structure blacks consist of strong pearllike aggregations held together by primary-valence bonds or whether their state of aggregation is of a weaker type which depends on secondary-valence forces. Since oil absorption determinations on the blacks themselves give good correlations with those properties of rubber attributed to structure[2] it is probable that the structure is not formed necessarily in the rubber matrix by flocculation but is present in the original black before compounding. Dobbin and Rossman[3] recently have demonstrated that structure blacks are fluffy and are difficult to densify by direct compression or pelletization processes. These investigators were able to destroy structure characteristics by prolonged ball-milling; this procedure caused higher bulk densities and a lowering of modulus in rubber. No changes in particle size, surface area, tensile strength, and resilience accompany this change in modulus.

Although the concept of structure is helpful in explaining high modulus, smooth-out, and low processing shrinkage, other rubber properties of these blacks such as tensile strength, abrasion resistance, resilience[4], and dynamic modulus[5] can be correlated with particle size and are not particularly affected by structure. It is apparent that, if such structure exists, it must consist of relatively weak particle-particle association which can restrict to a small degree the elastic properties of the raw rubber matrix and, to a much smaller degree, that of the cured rubber matrix without affecting those properties depending on the extent or degree of carbon particle-rubber matrix bonding. Thus high structure blacks may be considered as characterized by a nonuniformity of dispersion in rubber compared to nonstructure blacks, although both types of blacks may be relatively completely wetted by the rubber matrix.

EVALUATION OF CARBON BLACK STRUCTURE

Sweitzer and Goodrich[6] have defined a structure index of carbon blacks based on oil absorption and surface area measurements. This index gives an indication of structure but suffers from the inherent inaccuracy of oil absorption determinations. Variations in oil absorption values arise from the difficulty in estimating the end points; difficulties in maintaining a controlled degree of mechanical working of the oil-black mix; and may depend on the mechanical agitation the black has received prior to testing. Also it would be more satisfactory to measure a rubber property directly affected by structure than a property of an oil-black system.

Electron micrographs of carbon black cannot give any quantitative estimation of structure in rubber because the observations are not made usually in

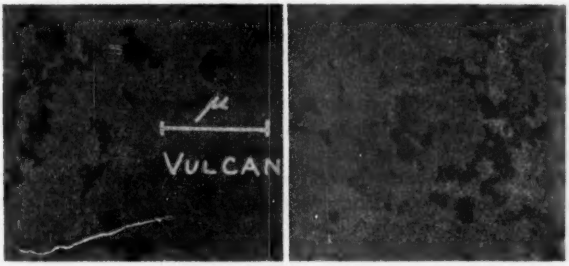

FIG. 1.—Electron micrographs showing results of different preparation of two samples of the same carbon black.

the actual rubber medium. Electron micrographs can vary in the degree of aggregation displayed, depending on the method of sample preparation employed, and also on the particular sample preparation under observation. Figure 1 illustrates this last point. Electron micrographs are shown of two sample preparations of the same black; both display some aggregates of high structure whereas other aggregates in the same pictures show lesser structure.

Differences in stiffness or modulus of loaded rubber stocks containing a series of blacks of approximately the same particle size is one of the experimental observations leading to the postulation of structure. The moduli for such a group of loaded stocks could be used as an index of structure. This procedure is not satisfactory because of the experimental difficulties involved in comparing moduli at equivalent states of cure, which is often an impossible condition to achieve. Even if this could be done, relative moduli ratings may vary with elongation, depending on the shape of the stress-strain curves.

Because of the large differences in mill shrinkage and smoothness of furnace black-loaded GR-S stocks, it was felt that such processing properties could be used to characterize these blacks. The practical utility of shrinkage measurements as a measure of rubber processing has been discussed in a number of publications[7].

It has been found that the effect of carbon black on processing shrinkage can be determined easily with a laboratory extruder equipped with a circular die. The data can be expressed as the shrinkage of a given weight of extruded stock or the equivalent expression of die swelling. Extrusion shrinkage is calculated from the difference in the length of extruded stock and the theoretical length calculated from the diameter of the die opening and the weight and specific gravity of the extruded section. This extrusion shrinkage value is related to die swelling by the following simple expression:

$$\% \text{ extrusion shrinkage} = \frac{100S}{S + 100}$$

where S is the percentage of die swelling.

Extrusion shrinkage measurements as described give about the same value as mill-shrinkage determinations and measure the same phenomenon of processing shrinkage.

METHOD FOR MEASURING EXTRUSION SHRINKAGE

The recipes given in Table I were used for all extrusion shrinkage measurements.

All mixing was done using a Type-B Banbury, followed by a 12-inch roll mill having a roll-speed ratio of 1 to 1.3. Batch factors of 5 for GR-S and 6 for natural rubber were used to determine the actual weight in grams of each batch.

The GR-S stocks were mixed in the Banbury using an 8-minute cycle followed by 3-minute roll-milling at a mill gap of 0.10 inch. The Banbury and roll-mill circulating water temperature was 120° F.

Natural rubber processing procedure consisted in mixing black, rubber, and softener in the Banbury using a 6-minute cycle. A zinc oxide-antioxidant masterbatch was added on the mill at a mill gap of 0.12-inch and the milling continued for 3 minutes.

Stocks were allowed to stand overnight at room temperature. After remilling these stocks and sheeting-off at a gap opening of 0.075-inch, strips

TABLE I

RECIPES USED FOR EXTRUSION SHRINKAGE MEASUREMENTS

GR-S		Natural rubber[a]	
Parts	Components	Parts	Components
100	GR-S	100	Smoked sheet
5	Bardol	3	Pine tar
3	Pine tar	3	Stearic acid
5	Zinc oxide	5	Zinc oxide
2	Sulfur[a]	1	Agerite Hipar
1	Santocure[a]	Varied	Carbon black
Varied	Carbon black		

[a] As a precaution against scorching the sulfur and accelerator were omitted at the 80 part loading in GR-S and at all loadings in natural rubber.

approximately 1 inch wide and 12 inches long were cut from the sheets in a direction across the milling grain. About 100 grams of these strips were fed into a No. 1/2 Royle extruder equipped with a die having a circular opening 0.109-inch diameter and heated by 168° F circulating water. The 100 grams of stock were recycled through the extruder three times; the last time care was taken not to stretch or pull the extruded section as it emerged from the die opening. Slightly over a meter length of the extruded section was cut off and placed on Holland cloth which had been lightly dusted with talc. After resting for a minimum of 4 hours a length of exactly 1 meter was cut off and weighed. The specific gravity of the stock was determined independently. For both recipes the specific gravity was 1.15 at a 50 part black loading. The extrusion shrinkage was calculated as follows:

$$\% \text{ extrusion shrinkage} = \left[1 - \frac{100\ (S.G.)\ (A)}{W} \right] 100$$

W = weight of 100 cm. of extruded stock in grams; A = area in square cm. of die opening; and $S.G.$ = specific gravity of stock.

Accurate temperature control of the extruder does not seem to be necessary in the case of GR-S. A variation in jacket-water temperature from 100° to 200° F caused a decrease of only a few per cent in extrusion shrinkage. Check values on a given GR-S recipe over a period of 6 months on separate mixings

TABLE II

SPHERON 9 EASY PROCESSING CARBON BLACK

Test No.	% Extrusion shrinkage	Deviation from average[a]
1	57.3	0.3
2	57.7	0.1
3	58.3	0.7
4	58.8	1.2
5	55.3	2.3
6	57.3	0.3
7	57.0	0.6
8	58.7	1.1
9	55.7	1.9
10	58.7	1.1
11	58.4	0.8
	Average 57.6	Average deviation 0.95

[a] % Average deviation = 1.65%; σ (standard deviation) = 1.14.

have shown excellent reproducibility. The data (Table II) on a 50 part loading of easy processing black in GR-S illustrate this point.

EXTRUSION SHRINKAGE OF REINFORCING FURNACE BLACK GR-S TREAD STOCKS

The above procedure was followed on a series of mixings in which the type of black and the loadings were varied. A more extensive study was made with GR-S than with the natural rubber mixtures because GR-S stocks give more information regarding the processing characteristics of carbon blacks. A few of the pertinent properties of the blacks selected for extrusion shrinkage evaluation are shown in Table III. These blacks cover a range of processing

TABLE III

PROPERTIES OF CARBON BLACKS FOR EXTRUSION SHRINKAGE EVALUATION

Trade name	Classification[a]	GR-S[b] Smooth-out	Surface area[c] (sq. m. per g.)	Electron microscope mean diameter (mμ)	Oil[d] absorption (lbs. per 100 lbs. black)
P-33	Fine thermal	Rough	15	134	40
Sterling-S	Semireinforcing	Rough	23	60	70
Spheron-9	Easy processing channel	Rough	100	33	81
Sterling-105	Reinforcing furnace	Fairly smooth	87	39	76
Philblack-O	Reinforcing furnace	Fairly smooth	75	33	110
Philblack-A	High modulus furnace	Smooth	43	..	116
Sterling-SO	High modulus furnace	Smooth	46	45	105
Kosmos-60	Reinforcing furnace	Smooth	90	35	110
Vulcan	Reinforcing furnace	Smooth	117	32	124

[a] Classification of carbon blacks is in a confused state at the present time due to the introduction of new furnace blacks possessing qualities not adequately characterized by any of the accepted classifications; all blacks possessing reinforcing properties about the equal of, or better than, easy processing channel black are shown as reinforcing furnace blacks; high modulus furnace blacks are less reinforcing than reinforcing furnace blacks but more reinforcing than semireinforcing.
[b] Appearance of 50-part loading tread recipe after extrusion.
[c] Low temperature nitrogen adsorption method[3].
[d] Gardner method[3].

properties. Fine thermal, semireinforcing furnace, and easy processing channel blacks were included to give a basis for comparison with the relatively new grades of reinforcing furnace blacks. The surface appearance of extruded GR-S stocks (Table III) is not related to either the surface areas or the mean particle diameters. However, oil absorption values do characterize the high structure smooth-out blacks; the higher values indicate smooth stocks.

Figure 2 illustrates the marked variations obtained in the extrusion shrinkage-loading curves. The effect of loading on shrinkage is almost negligible in the case of P-33 (fine thermal), a black characterized by large particle size, low oil absorption, and low modulus. The blacks having the largest effect on reducing shrinkage vary considerably in particle size, but have in common high oil absorption and high modulus, and impart to GR-S stocks a smooth surface appearance. The blacks falling between these two extreme types show varying ability in retarding shrinkage and are also intermediate in those properties

associated with structure. It is, therefore, suggested that such a processing shrinkage measurement affords a quantitative means of rating the structure properties of all carbon blacks.

The broken line in Figure 2, labeled the smooth-out line, has been drawn through the particular loading at which the surface of the stocks appeared to develop an arbitrary degree of smoothness. Those blacks having the maximum effect in reducing shrinkage are also the most effective for giving high surface smoothness at low loadings. The smooth-out line is not horizontal as

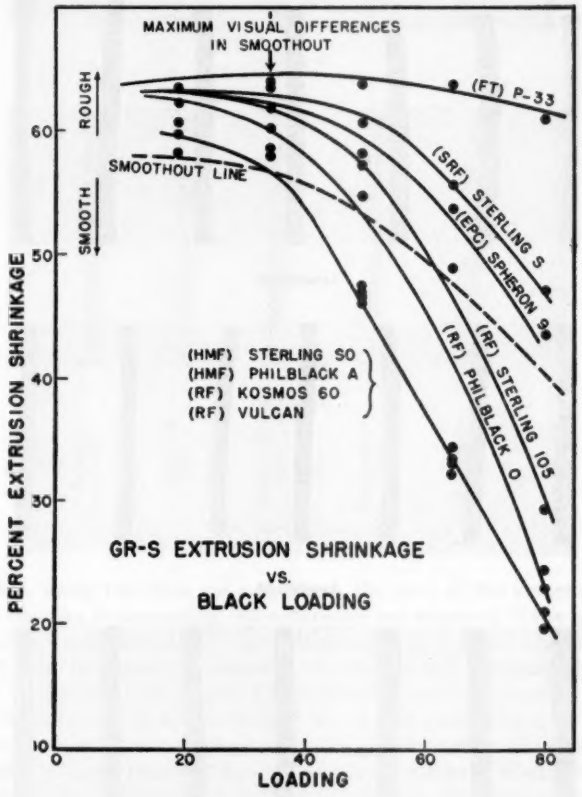

FIG. 2.

would be the case if shrinkage were the major factor responsible for surface smoothness. Considering the fact that one rubber stock showing an extrusion shrinkage of 50 per cent may be perfectly smooth, whereas another stock showing the same shrinkage may be rough, it must be concluded that smoothness is related to the uniformity of shrinkage. This uniformity of shrinkage seems to be another property associated with structure blacks.

The ability of structure blacks to reduce processing shrinkage may be explained possibly by assnmiug that the carbon particles are not dispersed

uniformly because of their original aggregation habit. This would cause variations in black concentration throughout the volume of the loaded rubber stock and result in a partial restriction of the elastic properties of the rubber matrix involved in the regions of higher black concentrations. Thus the same effect is produced as would be observed in going to a higher loading of black; the effective volume of the stock possessing elastic properties is reduced. This explanation therefore postulates a phenomenon similar to gel formation in the

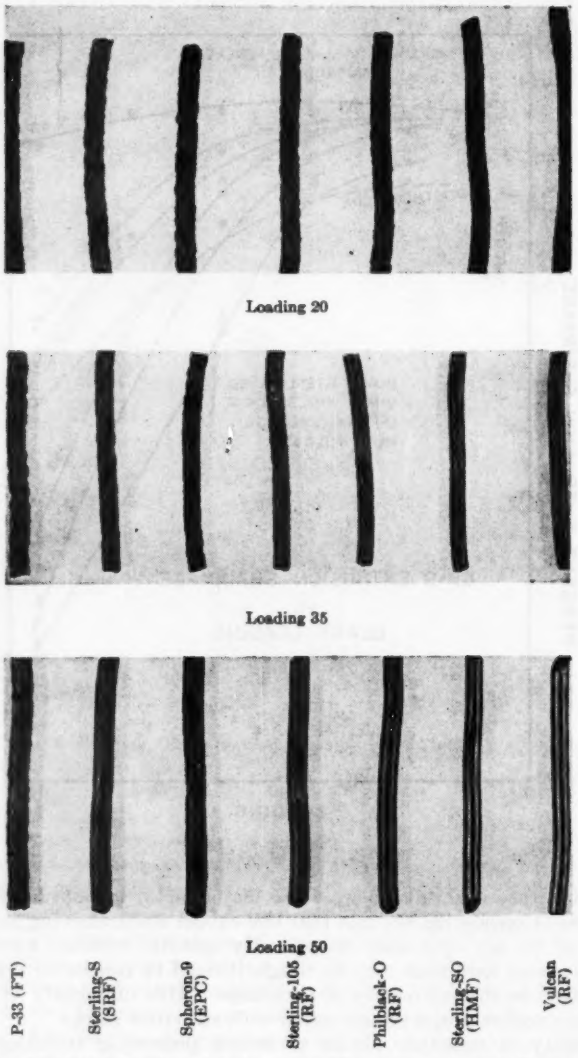

FIG. 3.—Extruded sections of stocks corresponding to curves shown in Figure 2.

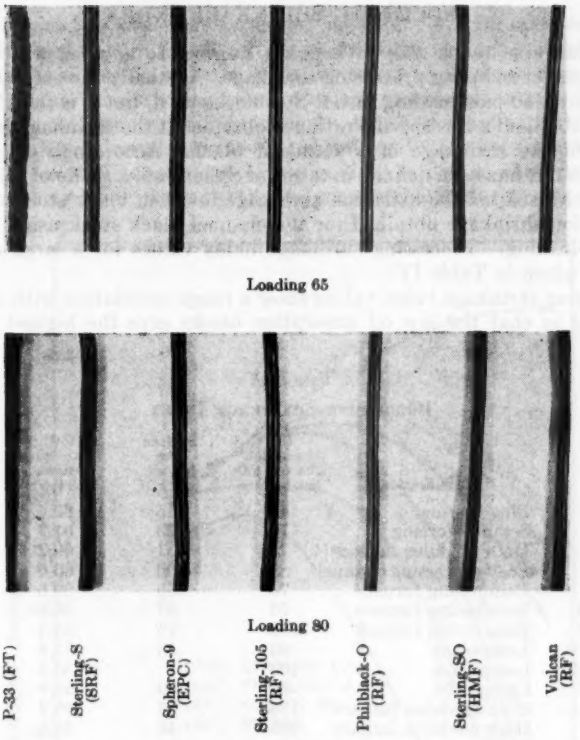

FIG. 3.—*Continued.*

rubber phase, using the term gel loosely, on the part of the structure blacks. Analogous changes in processing characteristics are observed if the gel content of standard GR-S is increased[10]. Deformation of such gelled systems is more irreversible than less restricted systems and results in a decrease of raw elasticity and processing shrinkage. These effects can be expressed in rubber chemistry terminology as a reduction of nerve. It follows that, if the above mechanism is correct, the rubber phase of the gelled fraction after deformation must be under a higher degree of strain than the remainder of the rubber matrix.

For comparing differences in surface smoothness it was found that at a 35-part loading the largest gradations were obtained. At the 20-part loadings all stocks were rough and at the 50-part loadings the smooth-out effect is so pronounced that small differences between blacks are obscured. Visual differences in roughness are easily recognized, whereas there are no differences apparent once a degree of high smoothness is obtained. Figure 3 shows extruded sections of the stocks corresponding to the curves shown in Figure 2. It is evident that smoothness increases with loading and that the structure blacks smooth out at lower loadings. The 35-part loadings have different surface textures for each section. This is not the case for any other loading.

PROCESSING SHRINKAGE INDEX

It is desirable to be able to assign a number to a black which rates its effectiveness for reducing processing shrinkage. Actually the extrusion shrinkage value at a 50-part loading in GR-S could be used, but it is felt that a more useful number and a less specific rating is obtained if the shrinkage is expressed in terms of the shrinkage of a standard black. Accordingly, a processing shrinkage index has been defined in terms of Spheron-9, a grade of easy processing channel black, as the extrusion shrinkage for each black stock divided by the extrusion shrinkage obtained for the channel black stock using GR-S and a 50 part-loading. Processing shrinkage index values for a large number of blacks are given in Table IV.

Processing shrinkage index values show a rough correlation with oil adsorption values in that the low oil absorption blacks give the highest shrinkage

TABLE IV

PROCESSING SHRINKAGE INDEX

Carbon black trade name	Classification	Oil absorption[a] (lbs. per 100 lbs. black)	Surface area (sq. m. per g.)[b]	GR-S, % extrusion shrinkage (50 parts)	Processing shrinkage index
P-33	Fine thermal	40	15	63.4	1.06
Sterling-S	Semireinforcing	70	23	61.7	1.03
Sterling-L	High modulus furnace	74	31	59.2	0.99
Spheron-9	Easy processing channel	81	100	60.0	1.00
Statex-K	Reinforcing furnace	75	55	59.6	0.99
Sterling-105	Reinforcing furnace	76	87	56.8	0.95
Philblack-O	Reinforcing furnace	110	75	54.5	0.91
Monsanto-10	Lampblack	93	13	51.8	0.84
Monsanto-B5	Lampblack	103	..	53.3	0.89
Monsanto-1	Lampblack	84	69	55.9	0.93
Philblack-A	High modulus furnace	116	43	46.2	0.77
Sterling-SO	High modulus furnace	105	46	46.8	0.78
Kosmos-60	Reinforcing furnace	110	90	46.9	0.78
Vulcan	Reinforcing furnace	124	117	45.7	0.76
Acetylene (Shawinigan)	Conductive furnace	144	65	41.6	0.69

[a] Gardner method[9].
[b] Nitrogen adsorption method[8].

and the high oil absorption blacks give the lowest shrinkage values. However, oil absorption cannot give a generally consistent index of processing because of the inaccuracy of the determination.

The samples of furnace blacks given in Table IV show two main groupings. One group has index values of 0.95 to 1.06 and is characterized by the processing shrinkage properties of channel black, although definite and reproducible differences exist in this group. The second group consists of high structure blacks in the narrow range of index values of 0.76 to 0.78. Philblack-O and the lampblacks are intermediate in shrinkage between these two extreme groups. Acetylene black gave the lowest processing shrinkage index in line with its high oil absorption value.

The decrease in processing shrinkage with an increase in black loading is expected simply from the fact that the volume of actual rubber in the stock is reduced proportionally. By expressing the percentage shrinkage on the basis of the volume of the rubber phase, where all the shrinkage occurs, interesting

loading relations are observed as shown in Figure 4. In each case except P-33, a definite maximum in rubber phase shrinkage value is evident. At the low loadings this shrinkage actually is increased by the presence of black, but at the higher loadings the effect of black structure reverses this trend. The loadings corresponding to the maximum values decrease with the effectiveness of the blacks in lowering processing shrinkage. It is felt that the increase in rubber phase shrinkage at the lower loadings is due to the greater strain imposed on the rubber phase by the presence of black during the process of

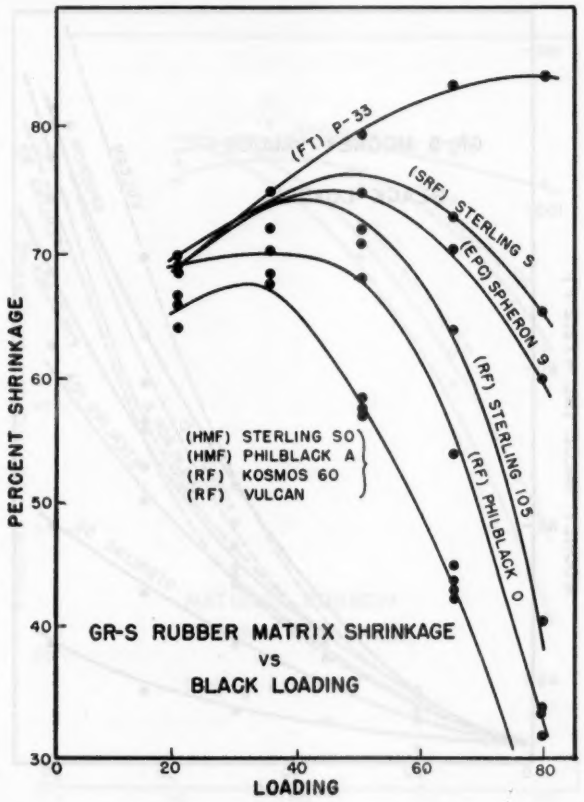

FIG. 4.

extrusion. On emerging from the die opening this enhanced strain causes a greater elastic retraction and higher shrinkage value. That the incorporation of carbon black causes the development of a higher degree of strain in the rubber phase on stretching has been demonstrated by x-ray studies of Gehman and Field[11]. As loading increases, the blacks, depending on their structure tendencies, overcome this effect of strain and restrict the elastic properties of the rubber phase. This retardation of elastic recovery caused by particle-particle association must freeze the rubber matrix in a state of higher strain than would be the case if blacks of lower structure had been used.

The effects of structure can be detected also from the variation of Mooney values with loading. Figure 5 shows curves of Mooney values against loading determined on the same stocks used in the extrusion shrinkage studies. The high structure blacks cause a sharper increase in Mooney values with increase loading than do the lower structure blacks. The plasticity of black-rubber stocks must, therefore, be a function of both particle size and the degree of black structure. Thus, structure tendencies of carbon black not only cause a reduction in the elasticity but also increase the plasticity of raw stocks.

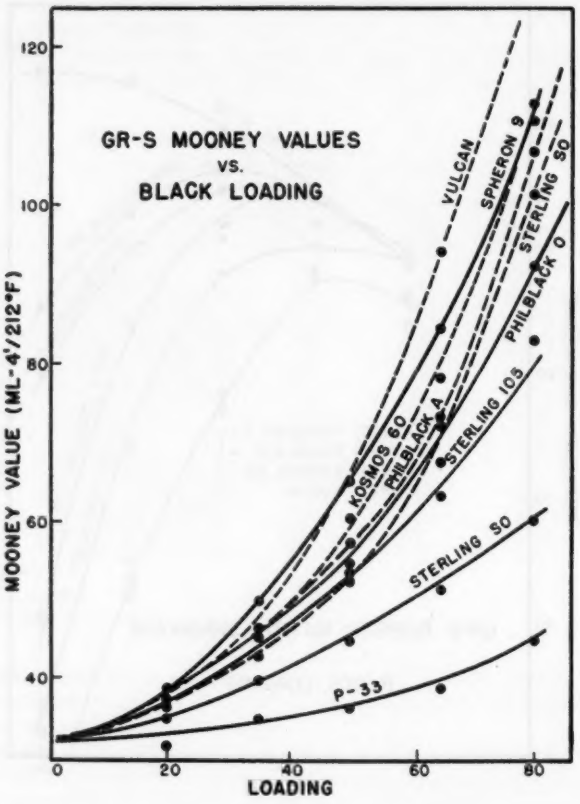

FIG. 5.

STRUCTURE FURNACE BLACKS IN NATURAL RUBBER

The processing properties of natural rubber stocks are much less affected by carbon black structure than is observed in the case of similarly loaded GR-S stocks. This probably arises from the greater mobility of natural rubber chain units compared to GR-S and the larger number of possible configurations of such units. A consequence of such a condition is enhanced rubberlike elasticity which would be less sensitive to restricting influences imposed by carbon black

structure. In Figure 6 it can be seen that at loadings of 50 to 80 parts of black the effect of structure in natural rubber is definitely present. The results correlate with those described for GR-S. However, at the 50-part loadings the range of extrusion shrinkage values from blacks of low to high structure tendencies is narrow compared to GR-S. At the higher loadings of 65 and 80 parts the spread becomes appreciable, but these loadings are not practical for routine evaluations of tread type recipes.

Since natural rubber is inherently smooth processing, the effect of black structure on this property is difficult to observe. Only at the 80-part loading

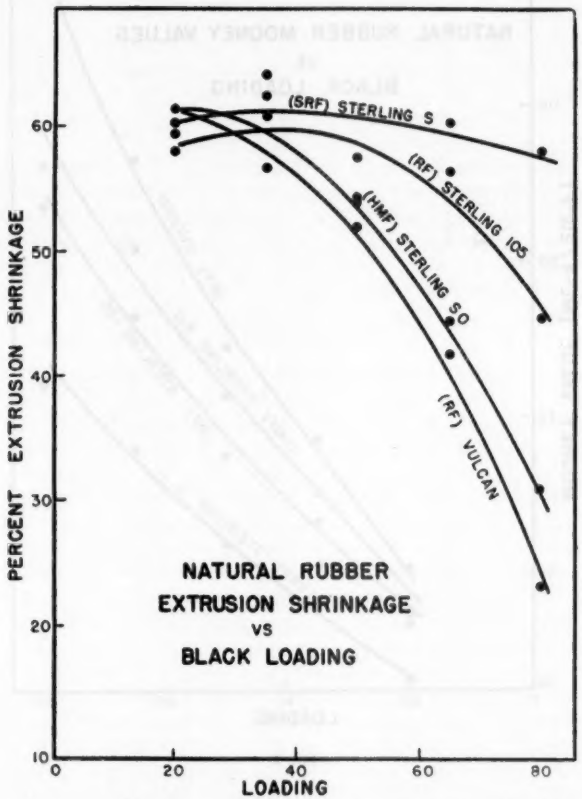

FIG. 6.

does there seem to be a definite effect of the structure blacks on the smoothness of extruded sections of natural rubber stocks. The reproducibility of extrusion shrinkage measurements with natural rubber also is not so good as with GR-S. Since the effects of milling, temperature, and oxygen are more pronounced with natural rubber than with GR-S, variability in processing shrinkage may be attributed to these factors. Because of the difficulties associated with

natural rubber, GR-S was selected as a more suitable rubber for characterizing the processing characteristics of furnace blacks.

Figure 7 shows the Mooney viscosity-loading curves for a few types of furnace blacks. In line with the extrusion shrinkage results in natural rubber, the structure blacks are not sharply differentiated from the other blacks. Sterling-SO, a definite smooth-out structure black, gives the same shape of curve as does Sterling-105, a black of much less structure. Only in the case

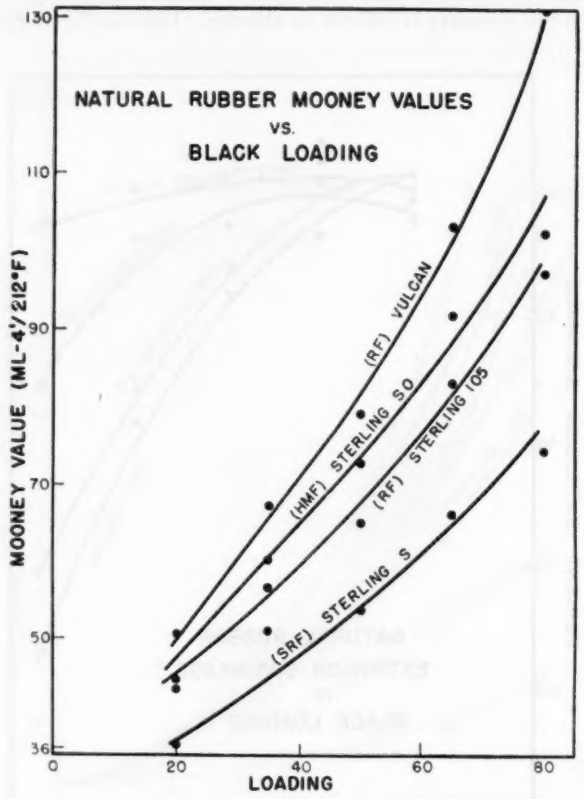

FIG. 7.

of Vulcan at the 65-part loading is a sharp increase in Mooney value observed. This black is a much smaller particle size black than Sterling-SO, and extrusion data place it in the same structure category.

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THE COMPOUNDING OF HARD RUBBER (NATURAL AND SYNTHETIC) *

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Hard rubber, frequently called ebonite, is a material which has many desirable physical and chemical properties. The relatively new plastics industry has offered stiff competition, yet it is reasonably safe to say that, for certain applications, nothing else can be substituted for hard rubber and still maintain its unique properties.

One of the principal qualities of this material is its finished appearance. When a high-grade ebonite compound is properly processed, it can be given a high lustrous finish which sets it apart from similar materials for beauty and richness. The highest grade of hard rubber is a compound containing only rubber and sulfur. It is in this type of compound that maximum physical properties and highest luster are found.

APPLICATIONS

The use of ebonite in specific applications depends, of course, on its physical and chemical properties. However, its attractive appearance has led to its use for articles wherein eye-appeal is as necessary as physical and chemical stability. Examples of such articles are combs, trays, toilet seats, steering wheels, pipe stems, drug sundries, bowling balls, etc. There are numerous other applications where the standard of appearance is not all-important, such as tank and pipe lining, battery cases, electrical parts, etc. For these uses, another inherent property is utilized, namely, chemical inertness. Hard rubber of almost any grade offers great resistance to chemical corrosion. For this reason, the hard rubber industry plays an important part in the chemical equipment field, where it is used extensively for lining tanks and pipes, for covering agitators, valves, fans, etc.

All of the aforementioned information is applicable to hard rubber made from both natural and synthetic rubber. Generally speaking, natural rubber is to be preferred, as it gives somewhat better physical properties. One important advantage of natural rubber is its ease of processing. Despite the great deal of work that has been done on improving the processing characteristics of synthetic rubber, *i.e.*, GR-S, the fact remains that natural rubber is easier to process than its synthetic counterpart. During the recent crude rubber shortage, however, various synthetic polymers were substituted very successfully, and it is probable that, in the future, synthetic rubber will be used for special applications. One difference between natural-rubber ebonite and synthetic-rubber ebonite is that a higher luster is obtained with the former. This property appears to be inherent in the polymer, but the difference is not too outstanding.

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SULFUR RATIOS

Strictly speaking, true hard rubber or ebonite contains 47 per cent of sulfur, and corresponds to the empirical formula $(C_5H_8S)_x$. Generally speaking, the term hard rubber includes compounds which contain at least 25 parts of sulfur per 100 parts of polymer, but even this designation is subject to qualification. Two factors affect the final state of the compound, *i.e.*, the sulfur ratio and the degree of vulcanization. For example, it is quite possible to cure two stocks, one containing 25 parts of sulfur and the other 45 parts, to the same state of cure, that is, possessing comparable physical properties. This is done by varying the time and temperature of vulcanization. In the industry itself,

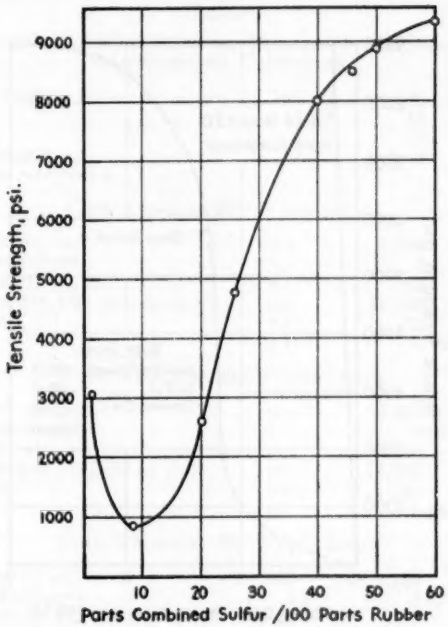

FIG. 1.—Effect of combined sulfur on tensile strength.

it is common to speak of a tank lining as being hard rubber when the physical properties might be 3000 lbs. per sq. in. tensile strength and 40 per cent elongation and the material itself in a flexible condition. Thus, the terms hard rubber or ebonite are used to mean a high-sulfur rigid material, cured to a state approaching its maximum. For material in the flexible, semirigid condition, the term semihard rubber will be used.

In Figure 1 the effect of combined sulfur on tensile strength is shown. The curve is an empirical one, drawn to show, in a general manner, what happens when the sulfur-rubber ratio is increased. A normal soft rubber compound is obtained with about 2 parts of sulfur. As the sulfur is increased to 8 to 10 parts, a degradation in physical properties occurs. With a further increase of sulfur to 20 to 25 parts a noticeable improvement in the tensile

strength occurs and the stock reaches the semihard flexible state, at which point it is actually undercured hard rubber.

When the sulfur is increased to 40 to 50 parts, the double bonds in the molecule become totally saturated, and the material attains the true hard rubber or ebonite state. At this point the tensile curve reaches a flat plateau and further increments of sulfur do not improve the tensile strength, due to the fact that the rubber molecule is fully saturated and, as has been pointed out, conforms to the empirical formula $(C_5H_8S)_x$, containing 47 per cent of combined sulfur.

Figure 2 shows the relationship between time of cure and tensile strength. It will be seen from the curve that the incorporation of 2 parts of an accelerator

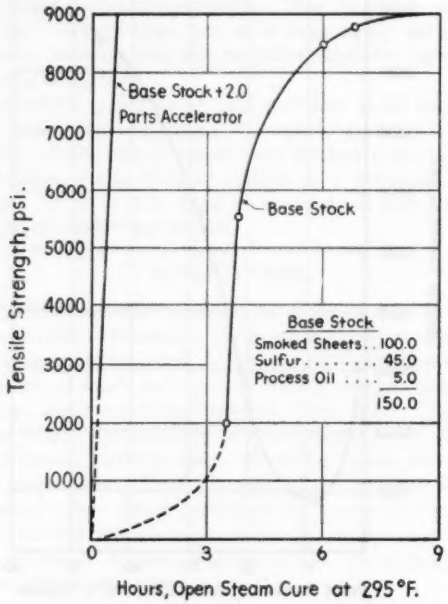

FIG. 2.—Relationship between time of cure and tensile strength.

reduces the curing time tremendously. It is important to note that, as shown in Table I, the physical properties are not reduced in any manner by this rapid type of cure.

COMPOUNDING FACTORS

Loading.—The most common fillers used in the compounding of hard rubber are hard-rubber dust, clay, whiting, wood flour, walnut shell flour, and silica. The reasons for using fillers are:

1. The cost of the compound is reduced.
2. Nonblowing cures can be obtained even with thick sections.
3. Shrinkage of the stock is greatly overcome.

4. Unloaded stocks cannot be molded satisfactorily without damaging the mold by molten sulfur.

5. Heavily loaded stocks possess greater dimensional stability, a very important factor in extrusion.

Of the fillers mentioned above, hard-rubber dust is considered to be the most satisfactory for making a high grade, low-gravity compound. However, since it is usually more expensive than the others mentioned, its use is not always economical. Whiting is a very good mineral filler, but it should not be used in applications where the compound is expected to have high acid

TABLE I

COMPARISON OF NONACCELERATED RUBBER-SULFUR STOCKS WITH ACCELERATED COMPOUNDS

Smoked-sheet rubber	100	100	100
Sulfur	45	45	45
Process oil	5	5	5
Thiuram accelerator	...	2	...
Aldehydeamine accelerator	...	...	2
Cure: 1 hour at 295° F open steam			
Tensile (lbs. per sq. in.)	n.c.	8,700	7,120
Elongation (percentage)	n.c.	3.4	3.1
Hardness (Shore D)	n.c.	87	82
Transverse strength (lbs. per sq. in.)	n.c.	13,500	10,400
Softening point (° C)	n.c.	62	51
Impact (Izod)	n.c.	0.92	0.64
Cure: 3 hours at 295° F open steam			
Tensile (lbs. per sq. in.)	n.c.	8,260	9,217
Elongation (percentage)	n.c.	3.07	4.1
Hardness (Shore D)	n.c.	90	87
Transverse strength (lbs. per sq. in.)	n.c.	14,600	14,290
Softening point (° C)	n.c.	64	71
Impact (Izod)	n.c.	0.86	0.81
Cure: 5 hours at 295° F open steam			
Tensile (lbs. per sq. in.)	8,520	9,100	9,240
Elongation (percentage)	3.4	3.95	4.3
Hardness (Shore D)	90	90	88
Transverse strength (lbs. per sq. in.)	13,600	17,300	14,400
Softening point (° C)	62	63	69
Impact (Izod)	0.87	0.93	0.71

n.c. = no cure.

resistance. Clays are also satisfactory except that they dry the stock, making it sometimes difficult to process. They also retard the cure considerably, especially if the stock contains reclaim. For compounds which must resist acid, the use of hard-rubber dust or silica is recommended. Wood flour and walnut shell flour are good fillers in molded compounds which must have a low gravity. They both retard the cure slightly in all-rubber stocks, but appear to have little effect when the compound contains reclaim. Carbon black does not reinforce hard rubber as it does soft rubber vulcanizates, and is seldom used as a filler. However, channel blacks of the EPC type are often used as coloring agents when a deep black color is desired in a cheap stock.

Activators.—Zinc oxide retards the vulcanization of hard rubber when it is present in any appreciable amount. It is useful, however, as a pigment in colored hard rubber stocks wherein the natural black color of the vulcanizate must be masked. Heavy calcined magnesia and lime are used as accelerator activators.

Acceleration.—It is the practice of some manufacturers of hard rubber to cure their products over a relatively long period of time without taking advantage of organic accelerators. There are several reasons which are claimed for this practice:

1. The long cures fit in with production schedules.
2. The use of accelerators increases the difficulty of separating scrap and flash rubber.
3. The use of accelerators introduces the hazard of scorching.
4. Maximum physical properties are obtained with rubber and sulfur only, vulcanized in a long cure. Some manufacturers seem to feel that the addition of any unnecessary ingredients tends to lower the physical properties of the vulcanizate.

The first two reasons are questions which must be decided by the individual factory. The scorching hazard is recognized as a definite problem, but with the proper precautions the damage can be held to a minimum. While it is true that maximum properties are obtained with rubber and sulfur only, as mentioned in reason 4 above, the use of organic accelerators does not in any way reduce these properties. This is shown in Table I.

The stock containing no accelerator was examined after one hour at 295° F, and no cure was evident. Even after three hours at 295° F, the stock was so undercured that its physical properties could not be measured. It is evident, then, that the incorporation of two parts of accelerator in the above base stock reduced the curing time from five hours to 1 hour. It is important to observe that there has been no reduction in physical properties due to the accelerated cure. For all practical purposes, the properties of the two stocks are identical.

The acceleration of hard-rubber vulcanization is essentially a means of reducing the curing time tremendously. It is our opinion that the time saved reflects great savings in power and labor costs; such savings are well worth the extra precautions necessary.

In general, the best accelerators for hard rubber are guanidines, aldehyde-amines, and thiurams. Guanidines are useful in curing thick sections of rubber where rapid acceleration is not necessary. Aldehydeamine accelerators should not be used in clay stocks because they retard the cure. In the case of very thick articles, such as bowling balls, the advisability of using rapid acceleration is questionable. The exothermic heat generated in such articles is tremendous and ultra-accelerators only aggravate the condition, causing further porosity. For such applications, the use of mild accelerators, such as the guanidines, is suggested.

Figure 3 shows the effect of thiuram accelerators on the rate of curing of a molded stock. It will be observed from the curves that a nonaccelerated stock of the given composition requires 90 minutes to reach the 6000 lbs. per sq. in. tensile strength. The same stock, to which has been added 2 parts of accelerator, takes only about one-third the time (34 minutes) to reach the same state of cure. Translated into factory processing, this means that merely by adding 2 parts of accelerator, the production of such hard rubber can be in-

creased three-fold. As is apparent from the curves, the time differential at higher tensile strengths is much more pronounced.

Antioxidants.—The use of antioxidants in hard rubber has been subjected to considerable discussion in the last few years, and the present concensus of opinion is that their use is not necessary. This conclusion is due to the fact that most hard-rubber articles are fully cured and are inherently resistant to oxidation, due to the nature of the vulcanizate. However, some electrical manufacturers favor the use of antioxidants, with the claim that a better

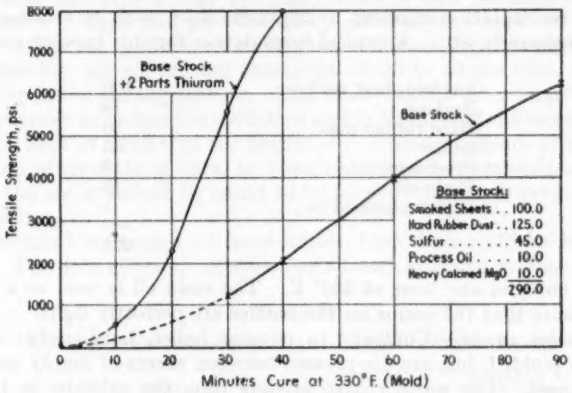

FIG. 3.—Effect of thiuram accelerators on the rate of curing of a molded stock.

surface is maintained, hence better electrical properties. A liberal quantity of antioxidant (3 to 4 parts/100 rubber) is recommended for stocks that are cured to the semihard rubber state, *e.g.*, semihard tank linings and semihard roll stocks.

SPECIFIC COMPOUNDING

General molded goods.—Some examples of hard-rubber molded goods are pipe stems, knife handles, gun butts, trays, etc. These articles are normally made from stocks of medium quality which contain a considerable amount of filler. Since it is necessary that they be manufactured on a mass production scale, acceleration is a universal method of obtaining rapid vulcanization. Following is a suggested formulation for general molded items:

Smoked-sheet rubber	50
Reclaim (50% RHC)	100
Sulfur	45
Hard rubber dust	200
Process oil	10
Heavy calcined magnesia	10
EPC carbon black	4
Tetramethylthiuram monosulfide	4
	423

This stock cures in 7 to 10 minutes at 330° F, provided the maximum thickness of the article in question is no greater than 0.5 inch.

There are two primary reasons for using such a large proportion of dust. First, it lowers the cost of the compound and, second, it reduces the shrinkage, producing a dead stock which flows easily in the mold. Because of the high quantity of dust used, the molded article is sometimes gray. For this reason the above formula contains a small proportion of channel black, which produces a dense black product. It might also be mentioned that, since hard-rubber dust has a comparatively low specific gravity, its use results in low-gravity compounds which are very often desired.

Hard-rubber acid bottles.—Acid bottles made from hard rubber are very often used for liquids containing hydrofluoric acid, such as etching solutions, frosting compounds, etc. A typical formulation for this type of compound is as follows:

Smoked-sheet rubber	100
Reclaim	15
Hard-rubber dust	50
Sulfur	45
Process oil	10
Rosin oil	10
Diphenylguanidine	1
	231

This stock cures in one hour at 330° F. The rosin oil is used as a tackifying agent to insure that the seams on the bottles are perfectly tight.

Hard-rubber combs.—Contrary to popular belief, hard-rubber combs are usually not molded, but are die-pressed between sheets of highly polished tin, and vulcanized. The warm rubber coming from the calender in the desired thickness is laminated between two sheets of tin. An automatic cutter cuts the sheets into suitable blanks, which are then die-pressed while hot. After vulcanization the tin is easily stripped from the cured blank, which then undergoes the further processes of grinding, teeth-sawing, and polishing. The following is a typical formula for a high grade comb:

Smoked-sheet rubber	100
Sulfur	45
Beeswax	2
Linseed oil	5
Accelerator (aldehydeamine type)	1.5
	153.5

This stock cures in hot water in 2 hours at 295° F. Some unaccelerated combs are made, but they require a cure of 8 to 9 hours at 295° F in water.

Tank and pipe linings.—Hard rubber is used for tank and pipe linings because of its great resistance to chemicals. This property is taken advantage of in acid-carrying tanks and in acid-conveying pipes, wherein the steel is lined with a hard-rubber compound; hence, the acid or other chemical cannot attack the steel. The general practice in lining chemical equipment is to cut the sheets of uncured rubber to size, using skived edges on all seams, then to cement the rubber to the steel. Finally, the entire assembly is vulcanized, usually in open steam. For some services a soft-rubber stock is veneered to the hard-rubber stock on the calender, and the rubber is cemented to the tank with the soft rubber next to the steel. The soft rubber acts as a cushion and is of value in absorbing sudden shock; it also reduces strains, due to the thermal expansion of the steel. Following is a formula which will make a representative tank

lining:

Smoked-sheet rubber	100
Reclaimed rubber	50
Hard-rubber dust	100
Process oil	10
Sulfur	40
Accelerator (aldehydeamine type)	3
Antioxidant (Neozone-A)	4
	307

Some tank and pipe linings are unaccelerated, and the cure runs 7 to 8 hours at 284° F. Tank and pipe linings are generally not cured to the ebonite stage, but rather are made in a semiflexible condition, *e.g.*, tensile strength of 4000 to 6000 lbs. per sq. in. and elongation of 20 to 40 per cent, to ease the strain of expansion during service. The incorporation of a large amount of antioxidant tends to reduce the oxidation and brittleness of the stock in service. It should be kept in mind that the degree of chemical resistance of hard rubber is a function of its state of cure, so when resistance to chemicals is the prime objective, the stock should be cured to as hard a state as is permissible with other requisites.

The chemical resistance of hard-rubber tank lining stocks is shown in Table II. The data given are intended as a rough guide only, since the specific

TABLE II

CHEMICAL RESISTANCE OF HARD-RUBBER LINING STOCKS

Solution	Resistance of hard rubber
Sulfuric acid (50%)	Excellent
Hydrochloric acid (concentrated)	Good
Glacial acetic acid	Fair
Phosphoric acid (85%)	Excellent
Nitric acid (16° Bé)	Fair
Nitric acid (35° Bé)	Very poor
Water	Excellent
Sodium hypochlorite (16%)	Good
Stannous chloride (15%)	Good
Sodium hydroxide (20%)	Excellent
Carbon bisulfide	Very poor
Benzene	Very poor
Chlorobenzene	Poor
Carbon tetrachloride	Poor

conditions of service, such as temperatures and concentration of the liquid, make it impossible to guarantee the chemical resistance of a tank lining under any or all conditions. The solutions shown are at room temperature.

It will be noted from the table that the organic solvents show a deleterious action. This condition is due to the swelling action of these materials. It has been shown[1] that the amount of organic liquid absorbed is a function of the combined-sulfur content of the vulcanized stock. Hence, the maximum resistance to organic liquids may be obtained by using an adequate amount of sulfur and curing to the maximum state consistent with the required physical properties.

Hard-rubber sheet.—The manufacture of hard-rubber sheet is a fairly large item in the industry; from such a material many articles are made. Sheets are made in various thicknesses, ranging from 0.030-inch to 3 and 4 inches. The uncured rubber is plied on the calender to the desired thickness, rolled between

sheets of highly polished tin, and then vulcanized in open steam or hot water, usually the latter. A typical formulation for a hard rubber sheet is:

Smoked-sheet rubber	100
Reclaim	30
Sulfur	50
Hard-rubber dust	150
Process oil	10
Tetramethylthiuram monosulfide	3
	343

A ½-inch sheet of this stock will cure in one hour at 295° F. Without acceleration, the cure will require 6 to 7 hours at the same temperature. If heat resistance is required, the use of 10 to 20 parts of aluminum-bronze or mica is recommended.

Rods and tubes.—From rods and tubes of hard rubber, many articles are prepared. To be of value, the hard-rubber stock must show two principal properties. First, the stock must be easily machined, and second, it must possess dimensional stability before cure. As a consequence of these requisites, hard-rubber rods and tubes are usually prepared from a heavily loaded nerve-free stock, such as the following:

Smoked-sheet rubber	100
Reclaimed rubber	20
Sulfur	50
Hard-rubber dust	200
Paraffin	10
Process oil	20
Accelerator (aldehydeamine type)	4
	404

After extrusion through an appropriate die, the rods are placed in soapstone and vulcanized. The tubes are generally placed on mandrels to prevent collapse and then cured in soapstone. The purpose of the soapstone is to prevent staining or water damage by the wet steam.

Hard-rubber battery boxes.—There are many types and grades of battery boxes, ranging from the poor quality asphaltic battery case to the very excellent hard-rubber grade used in such applications as submarine service. Following are typical formulas for two grades of hard rubber cases:

	High grade	Low grade
Smoked-sheet rubber	100	25
Reclaimed rubber	..	150
Sulfur	45	40
Hard-rubber dust	50	75
Channel black	..	4
Silica	..	100
Mineral rubber	..	50
Lime	5	10
Process oil	10	10
Accelerator (aldehydeamine type)	2	1
	212	465

These stocks cure in 20 minutes at 330° F when molded on a heated core. Some battery boxes are cured without acceleration for a long period of time, *e.g.*, 8 to 10 hours at 287° F in open steam. At the same temperature the addition of accelerator would reduce the time to approximately 3 hours. It

should be emphasized that, since battery boxes are used in acid service, the choice of filler is very important. Whiting, a very excellent cheap filler for molded items, should not be used in battery cases because of its low resistance to acid. Silica and hard-rubber dust are recommended as satisfactory fillers for this use.

Hard-rubber sponge.—Press-cured hard-rubber sponge may be made by the same general method employed for press-cured soft sponge. The following compounds are recommended:

Smoked-sheet rubber	100	100
Whiting	25	..
Sodium bicarbonate	10	20
Stearic acid	5	5
Mineral rubber	10	50
Sulfur	40	60
Accelerator (aldehydeamine type)	1	1
	191	236

Half-inch slabs of sponge made from the above compounds cure in 30 minutes at 90 pounds steam pressure (331° F). The first compound, containing whiting, averages about 27 lbs. per cu. ft.; the unloaded compound averages about 25 lbs. per cu. ft. The rubber for hard sponge should be very highly plasticized to obtain the maximum blow.

Some of the physical and electrical properties of high grade hard rubber are shown in Table III.

TABLE III

PHYSICAL AND ELECTRICAL PROPERTIES OF HIGH GRADE HARD RUBBER

Color	Jet black
Finish	High luster (when polished)
Tensile strength (lbs. per sq. in.)	8,000–10,000
Elongation at break (percentage)	4–6
Specific gravity	1.15–1.25
Heat distortion (° C)	55–65*
Transverse strength	12,000–15,000
Dielectric strength (volts per mm.)	50,000–60,000
Dielectric constant (1000 cycles per 5 volts)	2.8–3.0
Phase difference (1000 cycles)	0.25°–0.30°

* Special stocks have heat distortion points of 120° to 130° C.

FACTORY PROCESSES

Mixing.—The compounding of hard-rubber compounds is similar to that of soft rubber, the main differences being in the sulfur ratio and in the use of hard-rubber dust as a filler. The same equipment is used in fabricating hard rubber—mills, Banbury mixers, calenders, and extruders all being standard equipment.

BREAKDOWN OF ELASTOMER.—It is of vital importance in the fabrication of hard rubber that the raw elastomer be well broken down before it passes to the mixing operation. This requirement is doubly important for the synthetic elastomers, because they have considerably more nerve and show high shrinkage if not properly masticated. Natural rubber is more easily broken down and has much less nerve.

Briefly, there are two methods of mastication. One is on the conventional mill; the other is in the Banbury mixer. Of these two methods, the Banbury

mixer is to be preferred because of (1) its greater capacity and (2) the higher temperatures that are obtainable. It has been proved that a hot breakdown of elastomer is much more efficient than a cold breakdown.

INCORPORATION OF INGREDIENTS.—The most common ingredients in a typical hard-rubber compound are elastomer, sulfur, fillers, plasticizers, activators (such as magnesium oxide or lime), colors, and accelerators. Frequently reclaimed rubber is used to reduce costs and also as a processing aid. The order and methods of addition of these materials are very important in obtaining a good dispersion. The rubber reclaim should be added to the masticated polymer, either on a mill or in the Banbury mixer. This method insures a good dispersion of the rubber hydrocarbons before the other ingredients are added. It would be ideal if the other materials could be added separately too, but factory production schedules do not permit such a system. Therefore, the sulfur, filler, activator, plasticizer, and color are usually added together, all being uniformly stirred together by hand before addition. The mixing in of these ingredients is generally done on a cool mill in order to avoid any danger of scorching. It is important not to cut the rubber compounds on the rolls before the ingredients are all in, otherwise sulfur lumps are very likely to appear in the stock.

Accelerated stocks have to be treated very carefully in order to avoid scorching. There are several ways of handling these stocks:

(1) Add the accelerator separately on a cold mill after all the other ingredients are in. When thoroughly mixed, cut the stock from the mill and place on refrigerated tables until cool. Be sure to sheet these stocks out—do not roll up. Other means of keeping the stock cool are (1) to pass the material through a cold water spray and (2) to dip the stock into a cold water bath.

(2) Use accelerator masterbatches. This method is recommended for mixing accelerated stocks with a minimum of scorch damage. For stocks which may go through several processes, *e.g.*, calendering, extrusion, molding, the accelerator masterbatch can be withheld from the stock until the warm-up for the final operation. Thus, the danger of scorch is kept to a minimum. The use of accelerator masterbatches also results in a better dispersion of the accelerator throughout the entire stock.

STORAGE.—The storage of hard rubber batches can be carried out without much danger if the stock is not accelerated. In most cases, 24 hours' storage is recommended and it generally improves the quality of the finished product. This period of storage provides a resting period for the rubber compound which has so recently undergone terrific stress. Unaccelerated stocks can be rolled up and stored on racks until further use. Accelerated stocks must not be rolled up; rather, they should be sheeted out to cool.

Calendering.—The calendering of hard-rubber compounds is essentially no different from that of soft rubber. There may be variations in temperature, etc., but in general the methods are the same. For articles which are to be pressed and cured on tin, such as combs, trays, etc., stock coming from the calender in the desired thickness is calendered directly on to the tin, which is inserted underneath the rubber on the calender drum. A second sheet of tin is then rolled on to the top surface of the stock. Laminated structures, such as battery cases, are also made directly on the calender, the soft rubber laminate being calendered into the structure.

Molding.—The molding of hard-rubber articles is not a simple operation, and various precautions must be taken to obtain a solid, nonporous product.

The technique varies with the thickness of the piece to be molded—the thicker the piece, the more precautions one must observe. Most articles are molded from compounds which contain a large proportion of hard rubber dust. The dust has the effect of deadening the stock and preventing excessive shrinkage. A stock containing only rubber and sulfur cannot be molded satisfactorily, because the sulfur flows all over the mold, and the stock exhibits high shrinkage. Other fillers may be used, of course, but hard-rubber dust has proved to be most satisfactory. To avoid trapping air in the mold, it is customary to bump the press several times at the start of the cure, *i.e.*, raise and lower the ram of the press, thus opening the mold and allowing any air to escape.

Exothermic heat.—Exothermic heat may be defined as the heat evolved by the chemical combination of sulfur with an elastomer during the process of vulcanization. This heat is liberated at an early stage in the reaction, with consequent evolution of hydrogen sulfide, indicating that substitution, dehydrogenation, or decomposition is occurring. The amount of exothermic heat generated is a function of two quantities, as will be evident from the accompanying curves: (1) the temperature of vulcanization, and (2) the thickness of the specimen. In this study of exothermic heat, a typical medium quality molded stock was used. Following is the base formula:

Smoked-sheet rubber	100
Hard-rubber dust	125
Sulfur	45
Process oil	10
Heavy calcined magnesia	10
	290

The following accelerators were also tested, two parts of each being used: (1) tetramethylthiuram monosulfide, (2) piperidinium pentamethylenedithiocarbamate, and (3) aldehydeamine. The temperature readings were obtained by a recording potentiometer[2], with a range of 0 to 400° C. The thermocouples were of iron-constantan wires, with the ends slightly fused.

It has been claimed that the use of organic accelerators in curing hard rubber results in a magnification of the exothermic heat. The results of the present study show that this is not true, even with the fast accelerators used. What does happen is that the time of heat generation is advanced but the maximum temperature obtained is not affected. In Figure 4 the results show that the peak temperature is obtained at approximately 114 minutes for the accelerated stock, whereas in the unaccelerated stock the peak is not reached for 150 minutes. It is interesting to note that the three accelerators under discussion showed no appreciable differences in either the peak time or in the degree of generated heat.

Figure 5 shows the relationship between curing temperature and exothermic heat on a nonaccelerated stock. It is logical to assume that accelerated stocks would show the same characteristics. The results obtained in this study are in good agreement with those published by Winspear, Herrmann, Malm and Kemp[3]. Curing at 153° C resulted in a peak temperature of 245° C in 110 minutes, whereas at a curing temperature of 142° C the peak temperature obtained was 209° C at 190 minutes.

The effect of specimen thickness on the degree of exothermic heat is shown in Figure 6. As might be expected, the magnitude of the generated heat is a direct function of the thickness of the specimen. At two different curing temperatures, the curves obtained are similar in shape, the difference being

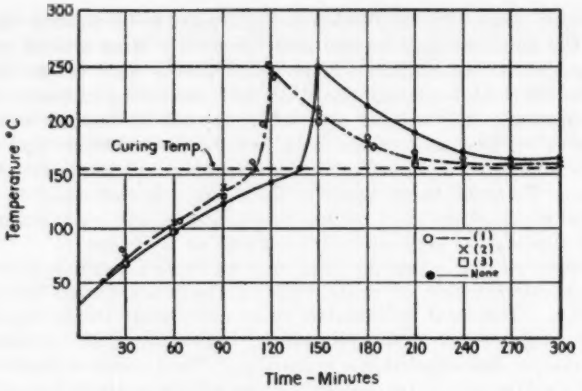

FIG. 4.—Exothermic heats of various accelerators—2-inch specimens. (1) Tetramethylthiuram monosulfide; (2) piperidinium pentamethylenedithiocarbamate; (3) aldehydeamine.

only in magnitude. In the case of the stock cured at 153° C, the exothermic heat does not become too great until a thickness of one inch is used. When the curing temperature is reduced to 142° C, the effect of the generated heat is not too apparent until a thickness of one and one-quarter inches is reached. Hence, these heating curves are of practical value in determining the degree of exothermic heat generated by a given thickness of sample; the necessary precautions can then be taken to avoid porosity.

To avoid any possible misunderstanding, it should be pointed out that there is no direct correlation between these exothermic heat curves and the usual time-tensile curves. The great differences in rate of curing between accelerated and nonaccelerated stocks shown in Figure 3 were obtained on specimens of ¼-inch thickness. On such a sample thickness, the effect of exothermic heat is negligible. In summation, it may be said that organic accelerators greatly increase the rate of curing (especially on thicknesses under one inch) and the use of such accelerators also increase the rate of generation of exothermic heat in samples of any thickness.

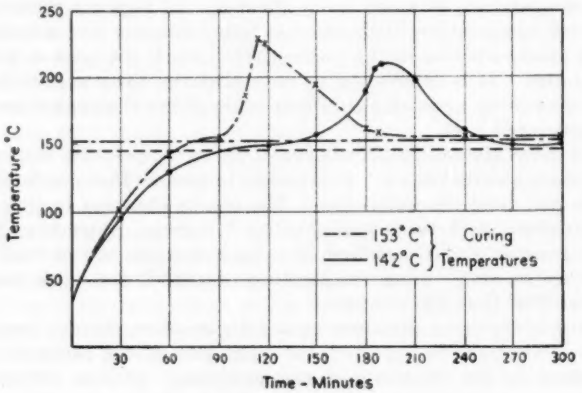

FIG. 5.—Effect of curing temperature on exothermic heat (unaccelerated stock—½-inch specimen).

Extrusion.—Extruded goods, like molded goods, must possess a similar degree of deadness or freedom from nerve. This condition is again arrived at by the addition of filler, usually hard-rubber dust. The most common articles made by the extrusion process are rods and tubes of various dimensions and for many purposes. In most cases, the extruded products do not undergo any more processing until they are vulcanized. Consequently, they must possess high dimensional stability, and it is for this reason that dead stocks are necessary.

Vulcanization processes.—The vulcanization of hard-rubber articles is similar to that of soft rubber, except in the length of the vulcanization period. The type of vulcanization used depends, as in soft rubber work, on the type of article and on the service to which it will be subjected. In general, there are three standard means of vulcanization, namely, open steam, water, and mold. These processes will be discussed separately and the type of compounds used in each will be shown.

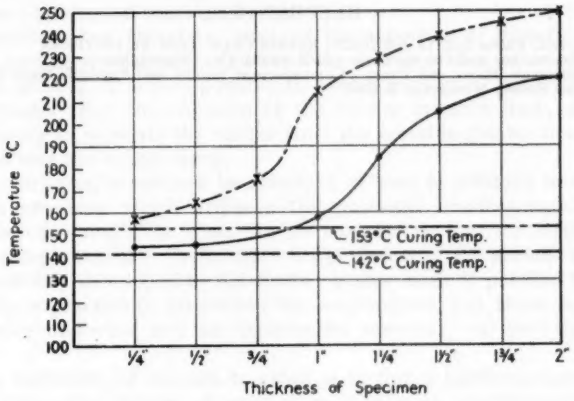

FIG. 6.—Effect of specimen thickness on exothermic heat (unaccelerated stock).

OPEN-STEAM VULCANIZATION.—This type of cure is used primarily for products which do not necessarily require a lustrous surface. Some examples of hard rubber articles which are cured in this process are battery cases, tank linings, rods, and tubes. The articles to be cured are placed in the vulcanizer and steam is introduced to the desired temperature. In some cases the products are packed in talc or soapstone to protect them from wet steam. Open steam cures generally have a cooling period after the cure is completed. The pressure is maintained by air while the steam is being withdrawn, thus precluding any blowing of the compound which might occur.

WATER-CURE PROCESS.—The curing of ebonite by means of hot water is quite commonplace throughout the industry. The water is heated by means of steam to temperatures well above its boiling point (the pressure of the steam above the water prohibits the boiling of the water). It is customary to press out articles for this type of cure between tin before vulcanization. For example, combs, trays, and high-grade sheet material are pressed between sheets of highly polished tin. After cure, the tin is stripped from the stock, leaving a very desirable finish on the article, which can be buffed up to a high lustre.

Articles which are not covered with tin may be vulcanized in hot water, but the water causes considerable staining on the exposed surface and the cured material is likely to be spongy due to water absorption.

MOLD VULCANIZATION.—This method of curing is very extensively used, and is the most efficient method of producing hard-rubber goods in quantity. Typical products cured in the mold are pipe stems, magneto parts, syringes, hard rubber pails, etc. Because of the high initial cost of a mold, the products from that mold must be manufactured by mass production. Since the molding cycle must be kept to a minimum, the rubber compound must be capable of rapid vulcanization, and that means one thing—acceleration. Practically all hard-rubber products produced by mold vulcanization are accelerated.

One common variation of mold vulcanization is to partially cure or set-cure the article in the mold, remove it from the mold, and then finish the cure in a hot air vulcanizer or jacket-heat. This method is used to speed up the production by decreasing the time that the rubber is in the mold.

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BONDING OF RUBBER TO METAL BY MEANS OF NEW CHEMICAL DERIVATIVES OF RUBBER *

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The bonding of soft rubber to a rigid surface is an industrial problem of great importance because only by having some means of bonding it to rigid materials is it possible to utilize the excellent damping properties of this material and to take advantage of its high resistance to various chemicals and utilize it as a protective coating.

This problem has, therefore, received the attention of investigators for a long time, and numerous methods have been developed for adhering rubber to metal. In general, it is now possible to obtain such good adhesion that it is actually greater than the cohesion of the rubber mixture itself, so that the force necessary to separate the rubber from the metal is greater than the force required to tear the rubber itself.

Satisfactory results can now be obtained, at least at ordinary temperatures, by certain processes which utilize a thermoplastic bonding agent, but the adhesion becomes negligible when the temperature reaches the softening point of the bonding material. Preliminary brass plating of the surface and certain methods recently developed in the United States make it possible to obtain a bond which is practically unaffected by temperature, but these methods call for expensive materials and an experienced operator, particularly in brass-plating.

It was, therefore, of interest to attempt to find a bonding material which would combine the virtues of ease of manipulation and strength of bond unaffected by thermoplasticity.

The literature on the bonding of rubber to metals is extensive, and a complete review has already been presented in previous publications[1], so only the chief methods which have found important industrial applications will be mentioned at this time.

The use of an auxiliary layer of ebonite to unite a soft rubber mixture to a metal surface is one of the oldest processes of bonding that is known and, in spite of its drawbacks, *e.g.*, the fragility of the ebonite, and the thermoplasticity of the latter, it is still used. Soft rubber mixtures do not adhere to iron but do adhere strongly to brass when the two are vulcanized in contact with each other. It is this observation which led to the process of brass-plating. A coating of brass is deposited on the metal, which serves as an intermediate link between the base metal and the rubber. Other methods involve the use of rubber derivatives as bonding agents between soft rubber and metal; *e.g.*, those methods which utilize Vulcalock, Ty-Ply, or chlorinated rubber.

Finally certain more recent products should be mentioned, with which excellent results have been obtained, but concerning which only fragmentary

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information is available with respect to possible applications and even to the nature or composition of the material. Among such materials may be mentioned, in particular, Reanite, Cycleweld, Meltbond, Pliobond, Redux, Lauxite, Vulcabond, Desmodur, and Durite. Information on some of these processes can be found in a recent publication of Génin[2].

PREPARATION OF RUBBER DERIVATIVES FOR USE AS BONDING AGENTS

It should be repeated that the purpose of an investigation of this kind was to develop a bonding process whereby an adhesion which was greater than the cohesion of the rubber mixture itself would be obtained, and which would not be thermoplastic, *i.e.*, would retain its properties even at high temperatures. Two different means of approach have been taken to this end:

(1) To start with a product already known for its bonding power and to modify its properties, particularly its thermoplasticity. This is the means of approach of Jarrijon and Louia[3] in experimenting with thermoprenes.

(2) To prepare a derivative of rubber containing groups which impart to it adhesive properties and which, by virtue of being vulcanizable, is no longer thermoplastic after being put into service.

Starting with this idea, Le Bras and Jarrijon[4] adapted to the bonding of rubber to metal, in conjunction with chlorinated rubber, the addition product of rubber and acrylonitrile studied by Compagnon and Delalande[5]. It is their results which induced the present author to undertake a more thorough study of the problem by investigating the effect on the adhesion of replacing acrylonitrile by ethylene compounds.

Compagnon and Delalande applied to various products, particularly acrylonitrile, the reaction of rubber with maleic anhydride described by Bacon and Farmer[6]. The method of these latter served as a starting point in the present investigation for the preparation of various derivatives, and these will be described in some detail.

Bacon and Farmer showed that when a solution of crude masticated rubber in toluene and maleic anhydride, in the presence of a small percentage of benzoyl peroxide as catalyst, was heated for several hours at about 100° C, a definite reaction took place, and that the product of this reaction could be precipitated by alcohol. By varying the experimental conditions, *e.g.*, the proportions of maleic anhydride and of benzoyl peroxide, the type of solvent, concentration of reagents, and time of heating, Bacon and Farmer obtained a whole series of addition products. The properties of these derivatives varied with the proportion of combined maleic anhydride which they contained.

Under certain conditions, Bacon and Farmer obtained soluble products; in fact to obtain them it is necessary only to exceed a concentration of 3 per cent, based on the rubber. In the present work the following solution was used:

	Grams	Molecular equivalent	
Crepe rubber	3	1	(isoprene residue)
Maleic anhydride	1.08	0.25	
Benzoyl peroxide	0.24	0.0025	
Toluene	100	—	

A known weight of rubber and the other reagents weighed in small ampoules are placed in a closed crystal glass tube. The tube is drawn out at

its upper end, and the solvent is poured in through the funnel-shaped end thus formed. The tube is then sealed by a blowpipe. By shaking the tube vigorously, the ampoules containing the reagents are broken. Agitation is then continued gently until the rubber is dissolved, and the tube is heated in an oil bath for 8 hours at 130° C. At the end of this time, the tube is opened, the product of the reaction is precipitated by alcohol, is washed with toluene, then with alcohol, and finally is dried.

To determine the amount of anhydride fixed, the product is weighed; knowing the original amount of rubber, the increase in weight is used for calculating, at least approximately, the amount of combined anhydride.

All the rubber derivatives which were studied in the present work were prepared by this technique. When the compound which combines with the

TABLE 1

Monomer	Crepe rubber (isoprene residue)	Monomer (molecules)	Benzoyl peroxide (molecules)	Toluene (molecules)	Heating conditions (Centigrade)	Hours	Combined monomer (parts in 100 parts of derivative)
Maleic anhydride	1	0.25	0.0025	27	130°	8	12
N-Methylmaleic imide	1	0.25	0.0025	27	130°	8	20.7
N-Propylmaleic imide	1	0.25	0.0025	27	130°	8	21
N-Butylmaleic imide	1	0.25	0.0025	27	130°	8	22.2
Methyl acrylate	1	0.25	0.0025	27	130°	8	8
Methyl methacrylate	1	0.25	0.0025	27	130°	8	10
Methacrylonitrile	1	1	0.0025	27	130°	8	11.2
Acrylonitrile	1	1	0.0025	27	130°	8	12.3

rubber contains an atom of nitrogen, it is possible to determine, with a high degree of precision by the Kjeldahl method, the amount of reagent which has combined.

Table 1 gives, in condensed form, the rubber derivatives which were prepared, the experimental conditions, and the proportion of monomer which combined with the rubber.

PRELIMINARY EXPERIMENTS ON BONDING WITH VARIOUS DERIVATIVES OF RUBBER

The standard method of the American Society for Testing Materials was used for testing the adhesion of rubber to metal.

All the derivatives which were prepared were vulcanizable with sulfur, and advantage was taken of this fact to reduce the thermoplasticity of the bond. The vulcanizing agents were added to solutions of the derivatives, and the same recipe was used for vulcanizing the derivative as for vulcanizing the soft rubber mixture itself, for, as is evident, vulcanization of the latter and of the bonding film ought to proceed under the same conditions.

The composition of the mixture used for the rubber derivatives was as follows:

Rubber derivative	100
Sulfur	2.5
Mercaptobenzothiazole	0.5
Benzothiazoyl disulfide	0.5
Zinc dimethyldithiocarbamate	0.1
Phenyl-β-naphthylamine	1
Zinc oxide	50

As a result of various experiments, the following technique was adopted. On pieces of sanded metal there were spread:

(1) a film of chlorinated rubber;
(2) a film of a mixture of chlorinated rubber and the rubber derivative;
(3) a film of the rubber derivative;
(4) a film of a solution of the soft rubber mixture.

Four solutions, all in benzene, had, therefore, to be prepared, and Table 2 gives their compositions and concentrations.

Each of the derivatives which was prepared was tested under these same conditions, so the results are strictly comparable.

TABLE 2

No.	Substance in benzene	Percentage concentration
1	Chlorinated rubber (mean viscosity)	10
2	Chlorinated rubber, 5 parts + rubber derivative 2 parts	20
3	Rubber derivative	10
4	Soft-rubber mixture	20

Table 3 summarizes the results obtained. The time of vulcanization, which was the same in all the tests, was 35 minutes at 152° C. The values are the average of six tests.

TABLE 3

Monomer combined with the rubber	Percentage of monomer combined	Resistance to separation (kg. per sq. cm.)
Maleic anhydride	12	13
N-Methylmaleic imide	20.7	40
N-Propylmaleic imide	21	0
N-Butylmaleic imide	22.2	0
Methyl acrylate	8	35
Methyl methacrylate	10	40
Methacrylonitrile	11.2	45
Acrylonitrile	12.3	50

Figure 1 shows these results in a more striking manner.

From these results, several conclusions may be drawn:

(1) Maleic anhydride is of no practical interest, since the adhesion obtained was weaker than that obtained by direct bonding on chlorinated rubber.

(2) The presence of a methyl group seems to have a favorable influence, since *N*-methylmaleic imide gave a rather good bond, and this is indicated also by the bonds obtained with methyl acrylate and with methyl methacrylate.

(3) A long chain carrying the methyl group seems to have an unfavorable effect.

(4) The CN group gives better results than the CH_3 group, but the simultaneous presence of the CN and CH_3 groups does not seem to result in any improvement.

Among the products tested, therefore, the rubber derivative with acrylonitrile proved itself to be the most satisfactory, and its application was consequently studied in detail.

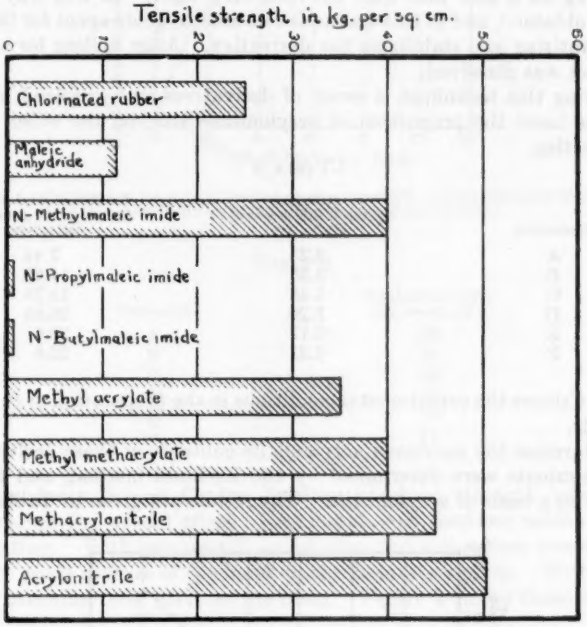

FIG. 1.

A DETAILED STUDY OF BONDING WITH THE RUBBER–ACRYLONITRILE DERIVATIVE

The preparation of the derivative in a sealed tube is tedious and requires a large quantity of solvent. To simply this, concentrated solutions were used, covering the range all the way to simple swelling of crepe rubber in toluene, in which the necessary acrylonitrile and benzoyl peroxide had already been dissolved.

After solution was complete, the mixtures were heated by first raising the temperature gradually during 30 minutes to 110° C, and then maintaining at 105–110° C for 2 hours. Under these conditions tenacious gels were formed,

TABLE 4

	Composition of solution				Conditions of heating		
Derivative	Crepe	Benzoyl peroxide	Toluene	Acrylonitrile	Time of rise (min.)	Time of curing (hrs.)	Temperature
A	100	8	250	10	30	2	110° C
B	100	8	250	20	30	2	110° C
C	100	8	250	40	30	2	110° C
D	100	8	250	60	30	2	110° C
E	100	8	250	40	30	5	110° C
F	100	8	250	40	30	9	110° C

which were broken up on a roll mill. The solvent can be recovered completely by ordinary methods.

The broken up mass of particles was agglomerated by first drying in hot air, then milling on a slow mill with the rolls very tight. In this way a smooth sheet was obtained, and to this was added an antioxygenic agent for the purpose of both peptizing and stabilizing the derivative. After milling for some time, the product was dissolved.

Following this technique, a series of derivatives was prepared by varying on the one hand the proportion of acrylonitrile and, on the other hand, the time of heating.

TABLE 5

Derivative	Nitrogen (grams in 100 grams of derivative)	Combined acrylonitrile (grams in 100 grams of derivative)
A	2.25	7.44
B	3.35	11.65
C	5.45	19.75
D	7.26	26.65
E	6.17	22.4
F	6.21	22.6

Table 4 shows the experimental conditions in the preparation of the different compounds.

To determine the combined acrylonitrile contents of these derivatives, the nitrogen contents were determined by the Kjeldahl method, and the values converted to a basis of acrylonitrile. The results are given in Table 5.

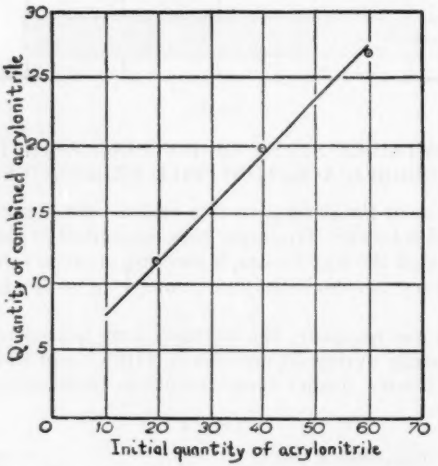

FIG. 2.—Influence of the initial quantity of acrylonitrile on the quantity of combined nitrile.

Figures 2 and 3 show, on the one hand, the relations between the quantity of combined acrylonitrile and the proportion of acrylonitrile originally, and, on the other hand, the time of heating.

A series of bonding tests were made in the usual way with each of the derivatives. The results, the averages of four tests, are shown in Table 6.

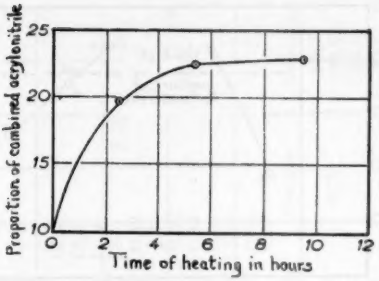

FIG. 3.—Influence of the time of heating on the proportion of combined acrylonitrile (the initial mixture contains 20 per cent of acrylonitrile).

TABLE 6

Derivative	Breaking strength (kg. per sq. cm.)
A	38
B	80
C	85
D	55
E	75
F	71

With products B and C, the limiting breaking strength was reached. Figure 3 shows the actual effect. The break was confined within the soft-rubber mixture. With products E and F also, the soft-rubber mixture broke, but in some parts rupture of the bond on the metal took place. With products A and D, breaking took place at the bond. Figure 4 shows these results.

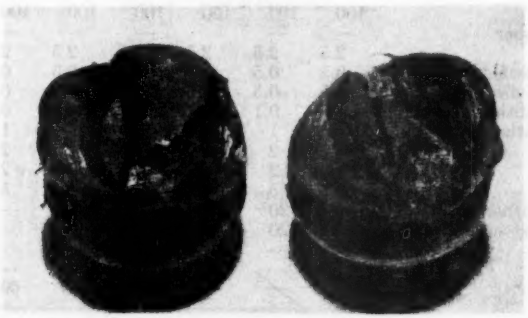

FIG. 4.—Test-specimens after having been ruptured.

In tests of the resistance to aging, samples subjected to various times of aging broke in all cases within the mass of soft rubber; hence aging of the actual bond was quite satisfactory. In tests of heat resistance, bond separation at different temperatures showed good bonds with rise in temperature, *e.g.*, at 110° C the strength was greater than 20 kg. per sq. cm.

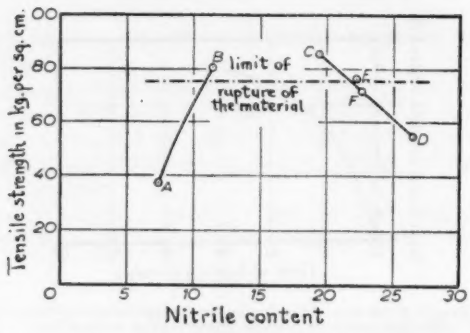

FIG. 5.—Influence of the nitrile content on the tensile strength.

GENERAL APPLICATION OF THE BONDING PROCESS

In the experiments which have been described, the tests were confined to one type of rubber mixture and to only one metal. To be certain that the process was of more general adaptation, further tests were carried out:

(1) with different types of rubber mixtures;
(2) with ferrous metals and light alloys;
(3) by bonding to plastics; and
(4) on coatings in open steam.

Tests with different rubber mixtures.—Table 7 gives the compositions of the mixtures tested, and the results obtained.

In all cases, rupture occurred within the mass of soft rubber.

TABLE 7

Ingredients								
Rubber	100	100	100	100	100	100	50	10
Reclaimed rubber	—	—	—	—	—	—	50	90
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Mercaptobenzothiazole	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Benzothiazoyl disulfide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc dimethyldithiocarbamate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phenyl-β-naphthylamine	1	1	1	1	1	1	1	1
Stearin	2	2	2	2	2	2	2	2
Pine tar	2	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5	5
Reënforcing carbon black	—	20	—	—	—	—	30	30
Semireënforcing carbon black	—	20	40	—	—	—	—	—
Whiting	—	—	—	60	—	—	—	—
Clay	—	—	—	—	60	—	—	—
Lithopone	—	—	—	—	—	60	—	—
Tensile strength (kg. per sq. cm.)	45	85	66	48	52	67	60	60

Tests with ferrous metals and various light alloys.—Table 8 gives the results obtained with various alloys[7], and the compositions as well.

In particular, the data in Table 8 show that a high nickel content in ferrous metals and a high percentage of silicon or magnesium in light alloys have an unfavorable influence on the strength of bond. It should be mentioned also that the adhesion on lead, zinc, nickel, aluminum bronze and carbon was

TABLE 8

		Breaking strength (kg. per sq. cm.)	Carbon	Silicon	Sulfur	Phosphorus	Manganese	Nickel	Chromium	Titanium	Molybdenum
Ferrous alloys	Extra-soft steel	85	0.2	trace	0.04	0.03	...	...	...	...	..
	Semi-hard steel	85	0.8	...	0.03	0.035	...	...	...	...	..
	Crominphy-2	45	0.3	0.2	....	....	0.5	0.5	12.5	...	..
	Arc-2706-A	20	0.1	0.3	....	....	0.5	9	18.3	...	..
	Arc-2266	20	0.1	0.3	....	....	0.4	8.9	17.9	...	2.8
	NS-20-S	25	0.1	...	....	....	...	9	18	0.25	..
	Imphy-DDD	83	0.08	0.21	0.019	0.003	0.43	0.17	0.14	...	..
	Imphy-MD	85	0.31	0.34	0.021	0.054	0.62	0.07	0.19	...	..
	Imphy-T	75	0.47	0.29	0.010	0.017	0.60	0.30	0.32	...	..
	N.A.	85	0.31	0.22	0.018	0.009	0.41	2.24	0.11	...	..
	NC-3H-2R	80	0.23	0.32	0.011	0.031	0.62	1.48	0.91	...	..
	Crominphy-1½	82	0.15	0.42	0.014	0.013	0.33	0.24	13.17	...	..
	NC-3H-1R	80	0.21	0.34	0.015	0.013	0.59	1.47	0.76	...	..

			Iron	Silicon	Copper	Magnesium	Manganese	Titanium	Aluminum
Light alloys	A-9	48	...	...	...	...	...	...	99.9
	AU-5-GT	60	0.20	0.30	4.60	0.25	trace	0.30	94.65
	AG-7	37	0.40	0.10	trace	6.80	0.50	...	92.2
	AG-5	55	0.25	0.23	0.10	5.3	0.40	...	93.7
	Ag-3	54	0.35	0.20	...	2.9	0.30	...	96.25
	AU-4G	56	0.40	0.30	3.90	0.60	0.50	...	94.3
	AS-13	29.5	0.60	13.2	...	...	...	...	86.2
	AS-46	50	0.50	4.0	...	0.50	0.70	...	94.3
	AM	54	0.50	0.50	...	...	1.25	...	97.75

excellent. The data obtained in these tests are, however, not included, since the tests were made with industrial products and not with standard test-specimens.

Bonding on plastic materials.—Tests were carried out on discs of thermo-setting plastic materials. Table 9 gives the results.

TABLE 9

Material	Result
Bakelite-A-77	Rupture of the plastic material
Paper coated with Bakelite	Stripping of the paper sheet
Cloth coated with Bakelite	Breaking of the screw clamps
Penmali (wood coated with Bakelite)	Rupture of the mixture at 75 kg. per sq. cm.

Tests with plyboard were unsuccessful because, during vulcanization, the moisture in the wood formed blisters in the rubber mixture and prevented adhesion.

As for Penmali (wood coated with Bakelite), only wood treated with cresol-formaldehyde resins gave satisfactory results. Wood impregnated with xylenol-formaldehyde resins became deformed during vulcanization as a result of softening of the resin.

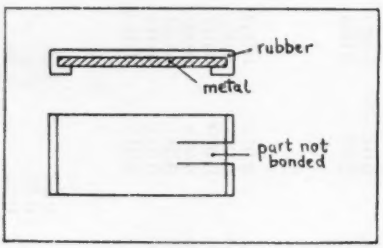

FIG. 6.

Coating tests.—Metal plates were faced with a layer of rubber to find out whether the process could be applied to small surfaces and whether good adhesion could be obtained without the application of the high pressures used in molding. In this work, metal plates 150 × 50 mm. were used. These were sand-blasted, coated with the desired solution, and a soft-rubber sheet, 0.5–0.7 mm. thick, was laid on, taking care to avoid trapping any air. The covered plates were placed in an autoclave and vulcanized in open steam.

TABLE 10

Material	Resistance to stripping
Iron	Very good (rupture of the soft rubber)
A-67	Very good (rupture of the soft rubber)
A-63	Very good (rupture of the soft rubber)
A-65	Very good (rupture of the soft rubber)
A-9	Good
AL-MN	Very good (rupture of the soft rubber)
AS-13	Poor
Paper treated with Bakelite	Very good (rupture of the soft rubber)
Penmali (wood treated with Bakelite)	Very good (rupture of the soft rubber)
Plexiglas	Good
Polyvinyl chloride	Fair

To measure the adhesion, a small tonguelike strip was cut in the rubber and a piece of cellophane placed under it so that there could be no adhesion. By pulling on the loose end of this strip, the strength of the bond could be estimated. Figure 6 shows this schematically.

The results obtained with various materials are summarized in Table 10.

In the case of polyvinyl chloride, the plasticizing agents had a tendency to exude and thus to impair the adhesion.

CONCLUSIONS

The bonding process which has been described is of general application to all types of rubber mixtures, to metals, and to various other materials, without any change in composition of the bonding agent for the different materials.

Although the problem of adhesion has been approached in this work only from the purely practical standpoint, it should be realized how little progress has been made in the theoretical knowledge of the problem. As a matter of fact, only a few authors have attempted to explain, on a basis of general concepts, certain special cases of adhesion, and there is still no real insight into the problem as a whole which might open the way to material progress.

If one turns to the works of MacBain[8], Delmonte[9], and Buchan[10] among the most important contributions to the phenomena of adhesion, the ultimate conclusion must be drawn that little has been accomplished in orienting investigations in this field toward more productive ends. From the physical point of view, particular attention must be paid to the condition of the state of the surface of the material to be bonded, to the surface tension, to the viscosity, and to the pH value of the adhesive. The chemical structure of the latter is that of a long-chain compound and, as has been proved conclusively in the present investigation, certain groups play a fundamental role, both in virtue of their chemical reactivity, and in virtue of the polar moment which they confer upon the molecule.

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COLOR REACTIONS OF SOME ACCELERATORS IN CURRENT USE *

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BERLIN, GERMANY

In taking an inventory, it was found that the labels on some accelerators had become lost, and the laboratory was called upon to identify the accelerators. However, little knowledge was available on this subject, so new analytical methods had to be developed. It was known that traces of copper can be detected by means of sodium diethyldithiocarbamate, the chemical nature of which bears a great resemblance to the compositions of Vulkazit-P, Vulkazit-P Extra-N, Vulkazit-774 and Thiuram. Hence it was to be expected that these accelerators would likewise react with copper salts. This was actually found to be the case. Encouraged by this success, a series of other accelerators were tested with the copper reagent, and it was found that every accelerator tested differed from all other accelerators in this reaction. This immediately offered a means of distinguishing some of the accelerators most widely used in the rubber industry.

Sodium diethyldithiocarbamate	$(H_5C_2)_2NC(:S)SNa$
Vulkazit-P	$H_{10}C_5NC(:S)SNH_2C_5H_{10}$
Vulkazit-774	$H_5C_2(H_{11}C_6)NC(:S)SNH(C_6H_{11})C_2H_5$
Vulkazit-P Extra-N	$[H_5C_2(H_5C_6)C(:S)S-]_2Zn$
Thiuram	$(H_3C)_2N(C:S)SC(:S)N(CH_3)_2$
Vulkazit-J	$H_3C(H_5C_6)NC(:S)SC(:S)N(C_6H_5)CH_3$

ACCELERATORS IN THE FREE STATE

The identification of accelerators as such can be carried out in water-insoluble solvents, such as carbon tetrachloride or methylene chloride, or in solvents such as acetone, which are miscible with water. The preferable type of solvent depends on the particular conditions.

Approximately 0.05 gram of accelerator is treated with 5 cc. of acetone; if solution is incomplete, the mixture is filtered, and 1 cc. of copper reagent is added to the filtrate. In the early experiments crystallized copper sulfate was used as reagent, in which case 2 grams was dissolved in 1 liter of water; this represented a copper content of 0.05 gram per 100 cc. of solution. In later experiments, lack of copper sulfate necessitated the use of crystallized copper acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$, in which case 2 grams in 1 liter of water gave a concentration of 0.06 grams of copper in 100 cc. of water.

When tested in this way, a series of accelerators gave characteristic reactions, as shown in the following data.

Vulkazit-P Extra-N $[H_5C_2(H_5C_6)NC(:S)S-]_2Zn$

Black-brown precipitate in a clear colorless solution.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk and Gummi*, Vol. 1, No. 6, pages 149–152, June 1948.

Vulkazit-P $H_{10}C_5NC(:S)SNH_2C_6H_{10}$

Chocolate-brown precipitate in a clear almost colorless solution.

Vulkazit-774 $H_5C_2(H_{11}C_6)NC(:S)SNH(C_6H_{11})C_2H_5$

First a greenish brown precipitate and turbid brownish colloidal solution; after 24 hours a black precipitate in a clear colorless solution.

Thiuram $(H_3C)_2NC(:S)SC(:S)N(CH_3)_2$

First a clear yellow-green, then dark olive-green solution; after 24 hours a black precipitate in clear colorless solution.

Vulkazit-J $H_3C(H_5C_6)NC(:S)SC(:S)N(C_6H_5)CH_3$

White voluminous precipitate, in colorless solution; this clear, supernatant solution soon turns intense yellow-green.

Merkapto $C_6H_4 \cdot N:C(SH) \cdot S$

Characteristic ochre-yellow flocculent precipitate in a turbid solution which is later clear and colorless.

Vulkazit-DM $[S \cdot C_6H_4 \cdot N:C \cdot S-]_2$

Light yellow flocculent precipitate.

Vulkazit-D $HN:C(NHC_6H_5)_2$

First a blue-green solution, which quickly becomes colorless, and forms a small amount of a slightly flocculent blue-green precipitate.

Vulkazit-H $HN \cdot CH_2 \cdot CH_2 \cdot NH \cdot C:C \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH$ (uncertain)

First a light blue turbid solution, which after 24 hours forms a bright blue to green-blue precipitate in a clear colorless solution.

Vulkazit-1000 $2,6\text{-}[HN:C(NH_2)NH]_2C_6H_3CH_3$

Clear violet solution.

Based on their chemical constitutions and their behavior with the copper reagent, the accelerators described above can be divided into groups; *e.g.*, the first three accelerators form a group by themselves; the following pairs of accelerators form in turn subdivisions, while Vulkazit-1000 stands alone. The first three accelerators give black-brown to black precipitates; this is true also of Thiuram, the initial yellow-green solution of which is characteristic also of Vulkazit-J, but in the latter case the precipitate is white.

Vulkazit-M and Vulkazit-DM, in accordance with their chemical constitutions, react in almost the same way with the copper reagent. Likewise the analogous behavior of Vulkazit-D and Vulkazit-H leads one to ascribe to Vulkazit-H the constitution shown. In view of its constitution and color reaction, Vulkazit-1000 stands apart from the other accelerators.

Vulkazit-CZ is a successor to the liquid accelerator Vulkazit-AZ, and is a gray or brown-gray powder having a neutral reaction. It contains sulfur, and its density is 1.34. When 0.05 gram is dissolved in 5 cc. of acetone, the

solution is filtered (this is somewhat difficult and a yellowish or brownish filtrate is obtained), and the filtrate is treated with 1 cc. of copper acetate reagent, the mixture becomes whitish and turbid, and a coarse flocculent gray-brown precipitate is formed, which settles rapidly.

The three accelerators, Merkapto, Vulkazit-DM, and Vulkazit-F, are difficult to distinguish by appearance, and their beige colors show only lighter or darker tones. Frequently Merkapto of a particularly light color is received in shipments. Their otherwise similar behavior made it necessary to find some other characteristic differences.

MERKAPTO

Vulkazit Merkapto (2-mercaptobenzothiazole) is readily soluble in acetone and, on treatment with copper reagent, the brown-yellow or ochre-yellow precipitate forms quickly and settles rapidly, leaving a clear yellowish supernatant solution. This reaction is characteristic of Merkapto.

When 0.1 g. of Merkapto is dissolved in 10 cc. of methylene chloride, in which it is readily soluble, the unfiltered solution agitated with 5 cc. of concentrated ammonium hydroxide, and the mixture allowed to stand, a colorless ammoniacal layer is formed over the methylene chloride. This serves to distinguish this accelerator from Vulkazit-DM and Vulkazit-F.

When a very small quantity of Merkapto is moistened with ethyl alcohol or with methyl alcohol on a watch glass, the resulting solution reacts acid to Merck indicator paper and Schering lyphan paper, as well as to litmus paper, in distinction to Vulkacit-F, which reacts basic, and to Vulkazit-DM, which reacts neutral or slightly acid.

When a filtered solution of Merkapto in acetone is treated with a little filtered aqueous solution of bismuth nitrate, an intense yellow coloration is obtained; with a much larger volume of bismuth nitrate solution, a rapidly settling yellow precipitate is formed. By this reaction Merkapto is clearly distinguished from Vulkazit-DM and from Vulkazit-F, which under the same conditions give first a whitish turbidity and then gray-white flocculent precipitates.

VULKAZIT-DM

Vulkazit-DM (benzothiazoyl disulfide) is in general more difficultly soluble than Merkapto. Its filtered acetone solutions react with copper reagent similarly to Merkapto, except that the precipitate is somewhat brighter yellow and the supernatant liquid is lighter, probably because of the lower solubility. Unlike Merkapto, the precipitate does not form immediately on addition of the copper reagent, but only after several hours; up to that time the solution remains turbid, in sharp distinction to the behavior of Merkapto. Still more characteristic, however, is the behavior of Vulkazit-DM in methylene chloride solution (unfiltered) with ammonia.

When 0.1 gram of Vulkazit-DM is dissolved in 10 cc. of methylene chloride and the solution, together with the insoluble residue, is agitated with 5 cc. of concentrated ammonium hydroxide, an intense reddish yellow or reddish brown-yellow ammoniacal layer forms over the methylene chloride solution. The insoluble residue, to the extent that it is not carried into the ammoniacal layer, forms a cloudy intermediate layer between the ammoniacal layer and the methylene chloride solution. After a considerable time, *i.e.*, days, the reddish tone disappears, leaving a more yellowish coloration.

Vulkazit-DM has a density of 1.45; when moistened with alcohol, it reacts neutral or slightly acid. With bismuth nitrate, its filtered acetone solutions give a whitish turbidity or precipitate.

VULKAZIT-F

Vulkazit-F has been designated by the I.G. Farbenindustrie as a combination of benzothiazoyl disulfide, *i.e.*, Vulkazit-DM, and a basic accelerator. Its density is reported to be 1.31. With copper reagent, its acetone solution gives a precipitate similar to that from Vulkazit-DM, except that the precipitate from Vulkazit-F forms more rapidly than from Vulkazit-DM. Likewise, in methylene chloride solution with ammonia, Vulkazit-F gives the same characteristic reaction as that of Vulkazit-DM, although the color is naturally only about half as intense as with the same quantity of Vulkazit-DM.

Vulkazit-F is easily wetted by water, and the solution foams when agitated, both phenomena depending on the basic component. When extracted with hot acetone in a Soxhlet, a reddish yellow solution is obtained, together with an insoluble beige colored residue. The latter has all the chemical properties of Vulkazit-DM; it represents about 60 per cent by weight of the Vulkazit-F; its acetone solution gives a turbidity with copper reagent and, only after a long time, is the precipitate characteristic of Vulkazit-DM obtained. When this is dissolved in methylene chloride, the reddish coloration characteristic of Vulkazit-DM is obtained with concentrated ammonia, and with bismuth nitrate solution an acetone solution of the residue gives a white precipitate. An alcoholic solution reacts neutral with Universal Merck indicator paper and with blue or red litmus paper.

From hot water solutions, reddish yellow needles crystallize. Their melting point is 177° C and they show an alkaline reaction. If the solution is concentrated, a reddish compound having the odor of urine and density of 1.19 is formed. This density is perhaps too low, for Vulkazit-DM is only slightly soluble in water and the solution reacts acid. The reddish water extract contains much sulfur and nitrogen, and with bismuth nitrate it gives a strong yellow color and a yellow precipitate, and it reacts alkaline.

Fifty parts by volume of Vulkazit-DM, of density 1.45, mixed with 50 parts by volume of the basic accelerator of density 1.17, gives 100 parts by volume of a mixture of density 1.31, *i.e.*, the density of Vulkazit-F. On a weight basis, this corresponds to 53.3 per cent of Vulkazit-DM and 44.7 per cent of the basic accelerator.

ACCELERATORS IN RUBBER MIXTURES

The identification of accelerators is of interest not only when they are in the free state but also when they are in rubber mixtures, particularly in vulcanized products. Accordingly master batches of accelerators[1], *i.e.*, mixtures of 5 parts of accelerator and 100 parts of natural rubber, were investigated[2]. In this work, the behavior of their acetone solutions was in most cases sufficient in itself to judge the type of accelerator present. The tests were carried out by treating 1 gram of master batch with 4 cc. of pure acetone, allowing to stand for about four hours, adding 1–2 cc. of 0.05 per cent copper sulfate solution, and observing the appearance of a color reaction, crystallization, or a precipitate, which would serve to distinguish and identify the accelerator present.

Accelerator (Vulkazit)	Reaction	
	Immediate	After 3 hours or longer
P Extra-N	black-brown almost clear solution	many long red-brown needles in a clear yellow solution
P	brown-yellow solution	many very small spear-shaped black needles in a clear yellow solution
774	green-yellow solution	many thick short black prisms and crystal druses in a clear yellow solution
Thiuram	yellow-green solution	many very fine long black needles in a clear yellow solution
J	yellow-green solution	many broad long red-brown needles and druses in a clear yellow solution
H	colorless solution	small amount of bright green precipitate in a clear colorless solution
D	colorless solution	pale blue-green precipitate in a clear pale yellow solution
Merkapto	yellowish solution	copious ochre-yellow precipitate in a pale yellowish solution
DM	yellowish solution	light yellow precipitate in a bright yellow solution
1000	pale blue-violet solution	small amount of purple crystal druses in a clear pale violet solution

Like Vulkazit-J, Vulkazit-P Extra-N gives red-brown needles, but the latter can be distinguished from the former by the black-brown solution which is first formed, in contrast to the yellow-green solution with Vulkazit-J.

To distinguish more clearly Vulkazit-774 from Thiuram, it is recommended to treat 1 gram of the master batch containing Thiuram with 3 cc. of pure chloroform, allow to stand 2 days, and then add 3 cc. of copper sulfate solution. After standing about 8 hours, the Thiuram accelerator shows a yellow-green diffusion which is characteristic of this accelerator. Vulkazit-J can be distinguished from Thiuram by its red-brown needles. To distinguish Merkapto from Vulkazit-DM, it is advisable to make the chloroform test as for Thiuram. In this case Merkapto gives an ochre-yellow color and Vulkazit-DM a white color. Tests with bismuth nitrate were not possible.

A light colored Buna mix heavily loaded with filler, and containing 36 per cent Buna and 0.3 per cent Merkapto, gave by immersion in acetone for 24 hours, an acetone solution which, with copper acetate solution, formed the ochre-yellow precipitate of Merkapto. At the same time 0.16 per cent of Vulkazit-D which was present was not manifest in the test. Since Vulkazit-D alone in acetone forms with the copper reagent only a slight precipitate, it is not surprising that amounts such as the 0.0016 gram in the test are hardly noticeable even if Vulkazit-D is recovered substantially unaltered in its active state.

The acetone extract of a black Buna mixing containing 54 per cent Buna and 0.35 per cent Vulkazit-CZ, obtained by immersion in acetone for 24 hours, gave with copper acetate solution a greenish gray to brownish gray precipitate, in accord with the normal reaction of Vulkazit-CZ alone.

It is evident that, even in Buna mixtures, accelerators can be identified by means of the copper reagent. Such mixtures should not remain in acetone too long, however, for too much phenyl-β-naphthylamine then passes into solution, and this gives such a strong coloration (reddish or yellow-brown) that the essential color reactions are disturbed.

It should be mentioned also that many accelerators, particularly when they are slightly soluble in water, show characteristic reactions when they are

brought in contact with the solution of copper salt. On the other hand, water-insoluble accelerators, such as Vulkazit-P Extra-N, Vulkazit-J, Merkapto, and Vulkazit-DM, do not react with the copper reagent. However, the practically water-insoluble Thiuram gives a characteristic yellow-green color with the copper salt solution. Vulkazit-P shows the chocolate-brown precipitate characteristic of this accelerator; Vulkazit-774 gives its brown-black precipitate; Vulkazit-D likewise gives its true blue-green precipitate; Vulkazit-H gives a green-blue precipitate; Vulkazit-1000 gives a turbid blue solution with violet sediment, and the hot water extract of Vulkazit-F gives with copper acetate solution an immediate coarse flocculent greenish blue precipitate, which settles rapidly.

The question as to what happens chemically to the accelerators during vulcanization remains unanswered. During this time they are exposed not only to high temperatures but also to the influence of molten sulfur, of zinc oxide, and of various other chemically active ingredients. As a result, many accelerators undergo changes during vulcanization, while others decrease in the amount still present, so in any case their identification is made more difficult than before vulcanization and requires different methods of analysis.

To examine the copper sulfate-acetone reaction for vulcanized rubber, experiments were carried out with a natural-rubber base mixture, containing no filler, of the following composition[3]:

Pale crepe rubber	100
Sulfur	1.5
Accelerator	1
Active zinc oxide	5

The time and temperature of vulcanization were different for the various accelerators, as shown in the tabulated results.

The light colored highly loaded Buna mixture already mentioned, which contained 36 per cent Buna and 0.3 per cent Merkapto, showed, after vulcanization and extraction with acetone for 24 hours, the following reaction. When treated with copper acetate solution, the acetone solution gave a yellow precipitate which was somewhat brighter than the precipitate normally obtained from Merkapto. Again the small accompanying amount of Vulkazit-D was hardly perceptible except for a greenish precipitate which in some cases was evident along with the yellow precipitate.

Also the black Buna mixture containing 54 per cent Buna and 0.35 per cent Vulkazit-CZ, which has already been mentioned, was likewise immersed in acetone for 24 hours, and the solution treated with copper acetate solution. A yellowish gray precipitate was formed, and this was lighter than that formed normally with Vulkazit-CZ.

Vulkazit-P Extra-N, Vulkazit-P, Vulkazit-774, Vulkazit-J, and Thiuram, recovered from vulcanizates, showed with the copper salt solution immediate black to light brown colorations in their acetone solutions, which remained clear or almost clear. The other accelerators, Merkapto, Vulkazit-DM, Vulkazit-D, Vulkazit-H, and Vulkazit-1000, showed, as the immediate effect, pale yellow to whitish turbidity.

Whereas Vulkazit-P Extra-N gives large red-brown crystals, Vulkazit-P forms microscopically small black needles, and Vulkazit-774 microscopically small black crystal platelets. This last accelerator behaves differently according to the conditions of vulcanization; after vulcanization for 15 minutes at 130° C, copper sulfate solution imparted only a black-brown coloration to the

Accelerator	Vulcanization	Immediate color	Later reaction	Solution
P Extra-N	10 min. at 120° C 15 min. at 130° C	black-brown	red-brown to dark brown large feathery and starlike needles and thick black needles	light yellow
P	10 min. at 120° C 15 min. at 120° C	yellow to black-brown	many microscopically small almost black needles	bright yellow
774	15 min. at 130° C self-vulcanized	black-brown	either only dark brown solution or light brown precipitate or black lamellar crystals	pale yellow
J	20 min. at 135° C 65 min. at 135° C	first black-brown then yellow-brown	many short thick black needles and red-brown starlets (closely resembling those from P Extra-N)	bright yellow
Thiuram	20 min. at 120° C 60 min. at 120° C	light brown	red-brown flocculent precipitate (very fine needles on the vulcanizate)	dark yellow
Merkapto	20 min. at 130° C 65 min. at 135° C	yellowish turbidity	ochre-yellow flocculent precipitate	colorless
DM	40 min. at 135° C 80 min. at 140° C	yellowish turbidity	yellow flocculent precipitate (brighter than that from Merkapto)	colorless
D	20 min. at 130° C 60 min. at 130° C	whitish turbidity	a little olive-green flocculent precipitate	bright yellow
H	60 min. at 135° C 80 min. at 140° C	slight turbidity	very little whitish compact precipitate	—
1000	20 min. at 135° C 60 min. at 140° C	whitish turbidity	vulcanizates exhibit a reddish shimmer, and often violet crystals	—

acetone solution, whereas, after spontaneous vulcanization at room temperature, a greeniwh brown precipitate was obtained, which on standing was transformed into black crystal platelets, with deposition of microscopically small crystal platelets on the vulcanizate itself.

A vulcanizate containing Vulkazit-774 which had been stored for 9 days gave, under the same conditions, only a very small amount of a flocculent precipitate, with a few small black points on the vulcanizate itself. This gave the impression that the accelerator had been entirely consumed.

Vulkazit-J, with its black and brown large and small needlelike and feathery as well as red-brown star-shaped crystals, resembles Vulkazit-P Extra-N in its behavior, but the immediate black-brown color of the acetone solution quickly changes to yellow-brown, and becomes pure yellow in the upper layer.

The red-brown flocculent precipitate from Thiuram is characteristic of this accelerator.

The precipitates from Merkapto and from Vulkazit-DM retained perfectly in these experiments their characteristic yellow color reactions.

In the case of the Buna vulcanizates, the yellow color of the precipitate was overshadowed in some cases by a greenish color, perhaps because of coprecipitation of the Vulkazit-D also present, which reacted greenish with the copper reagent.

Also Vulkazit-D followed its normal behavior, and gave only a small amount of a light green to olive-green precipitate.

Vulkazit-H gave only a whitish precipitate, and further experiments of a different nature will have to be carried out.

Even Vulkazit-1000 followed its normal behavior and formed characteristic violet crystals.

As is evident from the experiments which have been described, even after vulcanization the accelerators which were examined differ markedly from one another in their behavior with copper sulfate and acetone, so that their identification appears to be possible by this procedure.

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[1] These mixtures were kindly prepared by H. Budig.
[2] *Gummi-Ztg.* **55**, 849 (1941).
[3] *Gummi-Ztg.* **57**, 63 (1943).

THE ESTIMATION OF SMALL PERCENTAGES OF RUBBER IN FIBROUS MATERIALS *

C. M. Blow

The estimation of the percentage of rubber in fibrous products treated, for example, with Positex involves several difficulties, and no one method can be adopted on account of the difference in behavior of the various fibers. The fiber may consist of protein such as silk, wool or other animal fiber, and leather, or cellulosic material such as jute, cotton, rayon, paper, kapok, etc. The rubber may be vulcanized or unvulcanized. In addition to fiber and rubber, the presence of other substances such as soap, fats, waxes, oils, dyestuffs, fillers, pigments, etc., must not be overlooked. The problem of analysis appears complex, but may be simplified in some cases by knowing, from the process of manufacture, the definite absence or presence of certain ingredients.

The three techniques available are now discussed.

DESTRUCTION OF THE FIBER BY A CHEMICAL REAGENT WHICH IS WITHOUT EFFECT ON THE RUBBER

This method is applicable to protein material which is destroyed by boiling caustic soda, a reagent that does not affect rubber to any measurable extent.

The general method is to boil the weighed sample (1–2 grams) in about 30 cc. of 5 per cent caustic potash or soda until the fiber is completely destroyed (normally 10–15 minutes) and separate the rubber, dry, and weigh it. A 1 per cent solution for a longer time is recommended by some workers. Separation of the rubber sometimes presents difficulties. In the case of, say, a white woolen or worsted yarn, it is not usually difficult to filter the caustic soda solution through a No. 4 filter, *e.g.*, in a Gooch crucible with gentle suction, and wash, remove from the paper as a pellet, and dry.

Low quality woolen, *e.g.*, carpet yarns and heavily dyed materials, are often difficult or impossible to filter on account of finely divided gelatinous substances and (or) dyestuff. The method adopted is to centrifuge the caustic soda solution in a hand centrifuge, whereby the rubber rises to the surface and the nonrubber components sink. Both top and bottom layers are washed once or twice and recentrifuged to ensure complete separation. The rubber can usually then be easily collected and dried and weighed.

The same technique can be applied to leather-rubber compositions and real silk containing rubber, without any difficulties not encountered and dealt with above. A similar technique for cellulosic material, however, presents great difficulty in practice.

A number of "solvents" for cellulose have been tried, but the high viscosity makes separation of rubber difficult, particularly since the rubber may be in a fine state of division. The only method that appeared at all promising was to use boiling concentrated hydrochloric acid to break down the fiber structure. Using 1–2 grams of material, it was found that if the hydrochloric acid was

* Reprinted from The British Rubber Development Board Current Publications. This paper is Positex Pamphlet No. 7, published in September 1947.

decanted off through a sintered glass, or Alundum crucible, and the slurry of degraded fiber and rubber was shaken with 50 cc. of water and 10 cc. of benzene, the rubber (even if vulcanized) appeared in the benzene layer and the cellulose material could be separated off. Finally, the rubber was precipitated from the benzene by means of acetone, filtered, and weighed.

It is advisable in this method to add a small amount of oil-soluble dye to the benzene, if the rubber is not already dyed or pigmented, to make separation easier.

This method has been found satisfactory only for a good-quality cotton yarn containing up to 10 per cent of rubber. It is not simple, and some practice is necessary to judge the optimum amount of boiling, temperature to filter, and so on.

USE OF SOLVENTS TO REMOVE THE RUBBER WITHOUT AFFECTING THE FIBER

The percentage extract or percentage loss in weight of the material may be determined. Nitrobenzene (or *o*-nitroanisole) is used where large amounts of rubber, *e.g.*, mackintosh fabrics, have to be removed but it is not applicable in general to Positex-treated material.

Simple rubber solvents such as benzene, naphtha, and carbon tetrachloride are not reliable, since vulcanized rubber only swells in such solvents and is not completely extracted. In the case of unvulcanized rubber, removal is more complete, but the results need to be critically examined.

OXIDATION OR, MORE GENERALLY, CHEMICAL MODIFICATION OF THE RUBBER TO RENDER IT MORE READILY REMOVABLE FROM THE FIBER BY EXTRACTION WITH A SOLVENT OR BY EMULSIFICATION WITH A DETERGENT

The difficulty of destroying cellulosic material without affecting the rubber and the fact that simple extraction by solvents is slow and not always reliable have led to the development of a method of modifying the rubber chemically, *viz.*, oxidation, so that it can be readily removed from the fiber.

Oxidized rubber is dispersed or dissolved in caustic alkali and is soluble in acetone; furthermore, it has been found to be readily and completely removed from textile material by a simple soap and soda scour. To bring about oxidation, a catalyst is added. This may be cobalt or copper naphthenate, linoleate, or stearate, applied either as a dilute solution in carbon tetrachloride or benzene, or as a dilute emulsion in alkali, *e.g.*, ammonia; 1–2 per cent of the catalyst by weight on the dry material is required.

The following is a formula for a suitable emulsion:

Cobalt linoleate	10 grams
Sextol	20 cc.
Ammonia (1%)	20 cc.
Vulcastab-LS (1%)	5 cc.

Diluted to 1 liter for use.

If the material is finely divided and air can be made to reach all the surface readily, oven heating at 70° C for 1–2 hours is usually sufficient to oxidize it completely in the presence of the catalyst.

An an alternative, hydrogen peroxide appears the best oxidizing agent, since it leaves no residue to complicate subsequent determinations. The

rubber-containing material can be steeped in 20–40 times its weight of 3–5 volumes of H_2O_2, warmed to 50–60° C, and maintained there for 15–30 minutes; then, if necessary, filtered or evaporated to dryness before passing to the next stage, which is the separation of the fiber from the oxidized rubber.

We have two alternative methods:

First, as stated above, the oxidized rubber can be removed by boiling either with 1–2 per cent caustic soda solution or with dilute (0.1–0.2 per cent) sodium carbonate solution, with or without the addition of a small amount of sodium oleate. The rubber having been oxidized and dispersed, the fiber can be then collected, washed, dried, and weighed. Whether sodium hydroxide or sodium carbonate is used depends on the fiber involved.

Alternatively, the oxidized rubber can be extracted with acetone, after which the fiber or the extract can be weighed. It may be pointed out that, provided due attention is paid to the moisture content of the fiber, it is preferable to confine one's weighings to the fiber, since the rubber contains a rather indefinite percentage of oxygen.

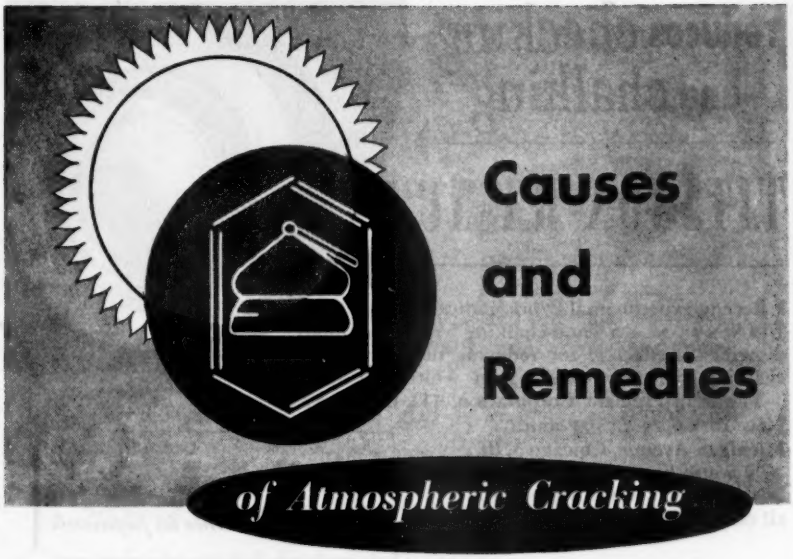
The material to be analyzed should be as finely ground or cut as possible. It should be noted that textile material takes up water in amounts related to the atmospheric humidity, and since this so-called regain may range from 0–20 per cent, this is an important point. Drying of all textile material at 90–100° C for 1–2 hours and weighing in closed vessels is perhaps the most satisfactory technique, the textile material after removal of rubber being similarly dried before weighing.

It is essential to acetone extract it before any determination. Acetone removes oils, fats and much of the waxes and organic dyestuffs and oxidized rubber, but does not affect unchanged rubber—vulcanized or unvulcanized. When a soap and soda scour or caustic soda treatment is to be given as part of the determination of rubber content, an alkaline water extraction is also necessary; protein, soaps, soluble coagulants, starches, etc., are thus removed.

In the case of rubber destruction methods, separation of the fiber from emulsified oxidized rubber may present problems. It is advantageous to centrifuge the solution to separate the fiber, which is subsequently washed (in the centrifuge), and then filtered. This latter separation can often be carried out in a Gooch crucible, using the fiber to form its own filtration pad. The fiber, after drying and weighing, is checked for purity by ash determination. Where the oxidized rubber is to be estimated by acetone extraction, the fiber can be filtered directly into the thimble.

The actone-insoluble and water-insoluble nonfiber and nonrubber components appear in the rubber in the case of fiber destruction methods and, therefore, the purity of the rubber must be checked by ash determination.

Corrections for added cobalt or copper salt must be made.



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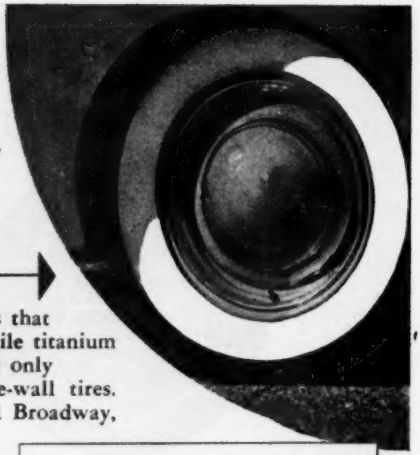

▶Recent experimental work indicates that TITANOX-RA-NC – a "non-chalking" rutile titanium dioxide – is effective for reducing not only chalking but also checking in white-wall tires.

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RECIPE

from the Barrett Rubber Research Laboratory

FOR

CUMAR*

RESIN, MH 2½ GRADE,

in Natural Rubber

The comparative data given here illustrate the excellent behavior of CUMAR* Resin, MH 2½ grade, when used as replacement material for 10 parts (weight basis) of natural rubber. It promotes smoother processing properties and lessens danger of scorching. It is an effective and economical extender for natural rubber, and contributes to the retention and/or improvement of significant physical properties. Where better tear resistance is required, it is exceptionally useful. CUMAR* Resin, MH 2½ grade, has found wide application in molded and extruded compounds used in the automotive and aviation industries, in footwear, soles and heels, flooring, drug sundries and household goods, mechanicals and insulated wire stocks, cements and adhesives, in white and light-colored items, and in non-staining and non-migrating compounds for uses involving contact with lacquers and enamels.

RECIPE

Smoked Sheets	100.0	90.0
CUMAR* Resin, MH 2½ grade	....	10.0
Calcium Carbonate (Precipitated)	75.0	75.0
Zinc Oxide	5.0	5.0
Stearic Acid	2.0	2.0
"AMINOX"	1.0	1.0
Sulfur	3.0	3.0
Benzothiazyl Disulfide	1.0	1.0
Total	**187.0**	**187.0**
Specific Gravity	1.31	1.33
Rubber Hydrocarbon, % by weight	53.5	48.2
Rubber Hydrocarbon, % by volume	76.0	69.5
Mooney Viscosity, ML, 4 min. @ 212 F.	10	19

Mooney Scorch, ML, 250 F.

Minutes	Viscosity	
1	10	17
5	8	13
10	8	12
15	11	13
20	65	14

Press Cure @ 307 F. (60 lb.) — 10 minutes

	Unaged	Aged 14 Days @ 70 C.	Unaged	Aged 14 Days @ 70 C.
Tension and Hardness Data				
Stress, 300%, psi.	600	850	500	750
Stress, 500%, psi.	1600	2200	1500	2050
Tensile, psi.	3250	2600	3300	3100
Elongation, %	680	550	730	630
Permanent Set, %	26	19	34	33
Hardness, Shore A.	50	56	46	52
Tear Resistance, Angle, Pounds per One Inch Thickness	215	200	250	245
Press Cure @ 307 F. (60 lb.) — 15 minutes				
Abrasion Resistance, DuPont	....	480	....	470
Compression Set, 40% Constant Deflection, %	26.8	....	27.3	....
Resilience, Yerzley, %	86.0	92.5	80.5	88.0
Rebound, Goodyear-Healey, %	73.5	81.1	72.3	78.7

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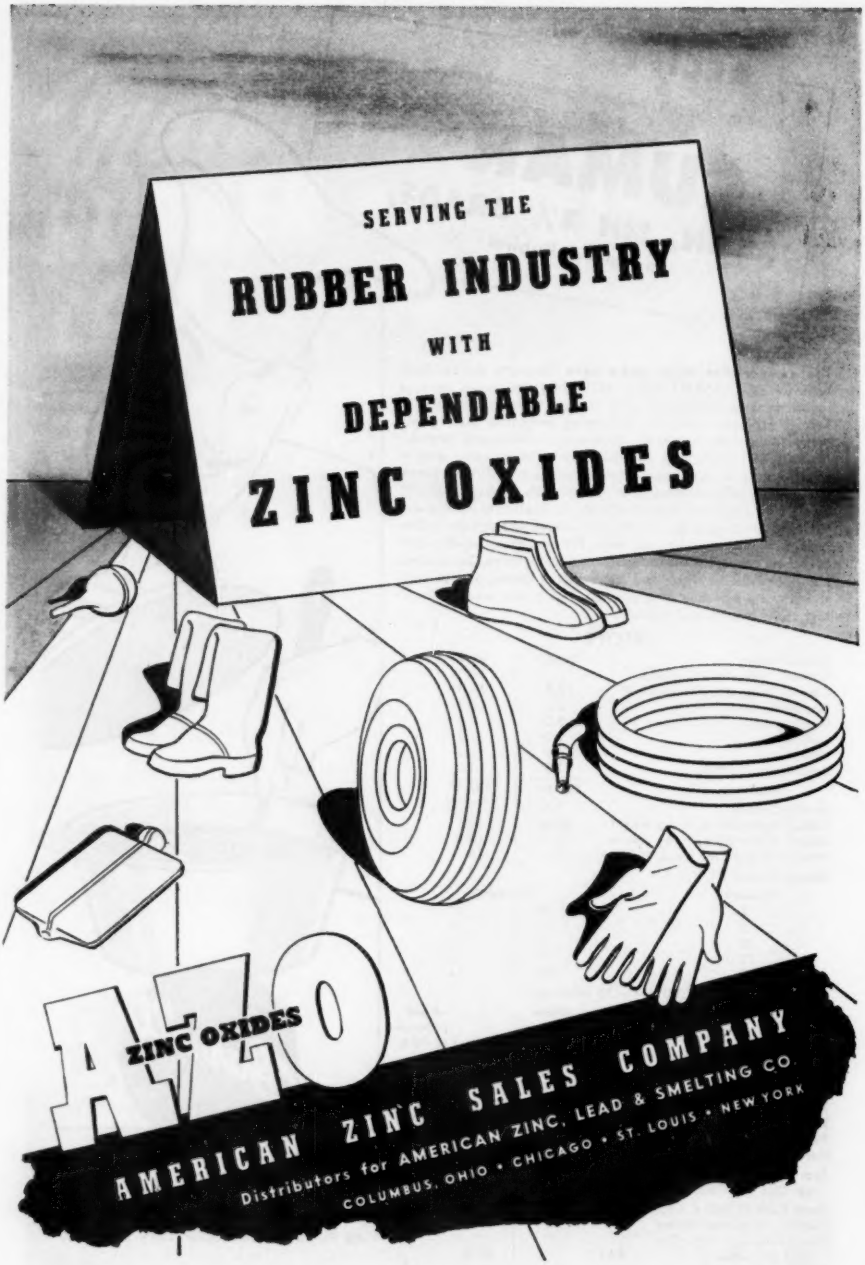
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The accompanying data show the compression set properties of similarly loaded Neoprene Type W and natural rubber stocks. Note that the rubber stock is especially compounded for low set. The data prove that the Type W stock is superior to the rubber compound at both 158° F. and 212° F.

This property alone means a tighter seal that retains its effectiveness over longer periods. Coupled with the other advantages inherent in all neoprenes—outstanding resistance to oils and chemicals, heat, sunlight, oxidation and abrasion—it assures a better product.

For more complete information on Neoprene Type W, consult Report 49-3. Extra copies are available. Samples of Type W will be sent on request. Ask your Du Pont representative, or write:

E. I. du Pont de Nemours & Co. (Inc.), Rubber Chemicals Division, Wilmington 98, Delaware.

• • •

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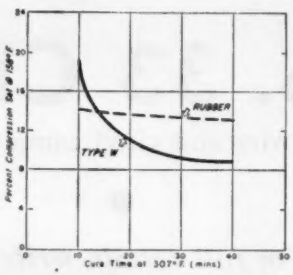
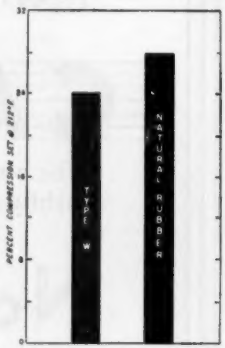
TEST RECIPES

NEOPRENE TYPE W	100.0	—
Smoked Sheets	—	100.0
NEOZONE A	2.0	2.0
Stearic Acid	0.5	3.0
Ex. Lt. Cal. Magnesia	2.0	—
SRF Carbon Black	29.0	39.0
Sulfur	—	0.5
PERMALUX	0.5	—
THIURAM E	—	2.5
Zinc Oxide	5.0	5.0





ABOVE—Compression set at 30% constant deflection, 70 hours at 212° F. Specimens cured 25 min. at 307°F.

LEFT—Compression set at 30% constant deflection, 22 hours at 158°F.

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For broad use with maximum economy, "Ludox" colloidal silica comes to you as an aqueous 30% colloidal solution of almost pure silica particles, less than 1/1,000,000 inch in size. Here are a few examples of how it can improve your products:

DIPPED GOODS: Greatly increased modulus and abrasion resistance and reduced water swelling are obtained when "Ludox" is added to neoprene compounds. It can be used to prepare excellent dips that will not settle or adversely affect the color of pigmented films.

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SATURANTS: Outstanding increases in tensile strength, abrasion resistance and internal bond strength can be obtained by adding "Ludox" to neoprene paper saturants. And it generally reduces water sensitivity.

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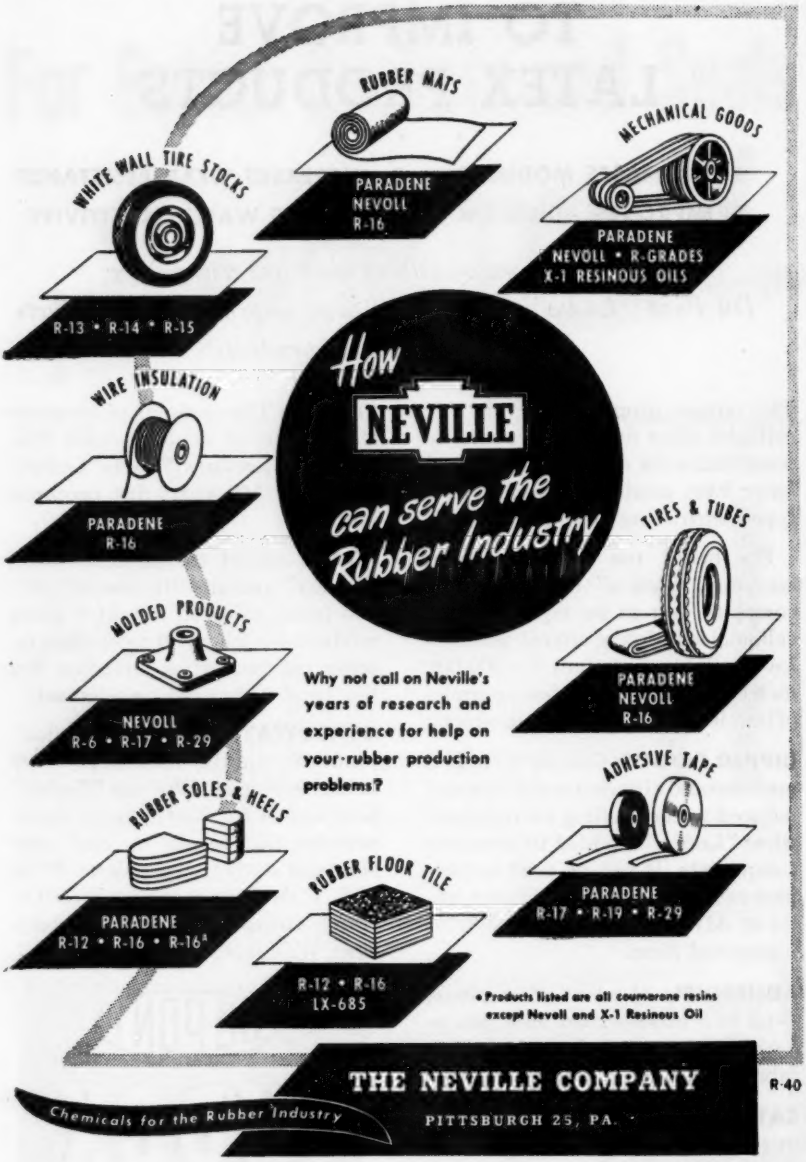
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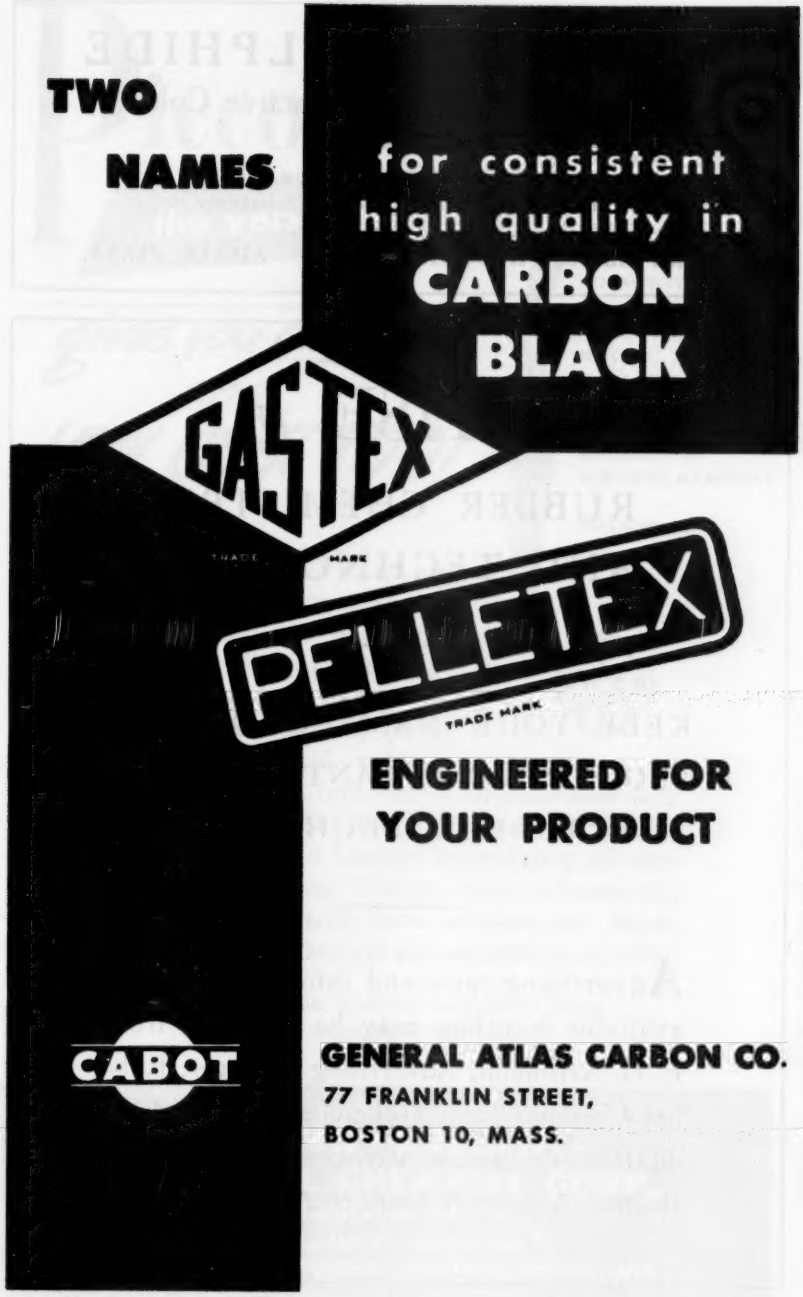
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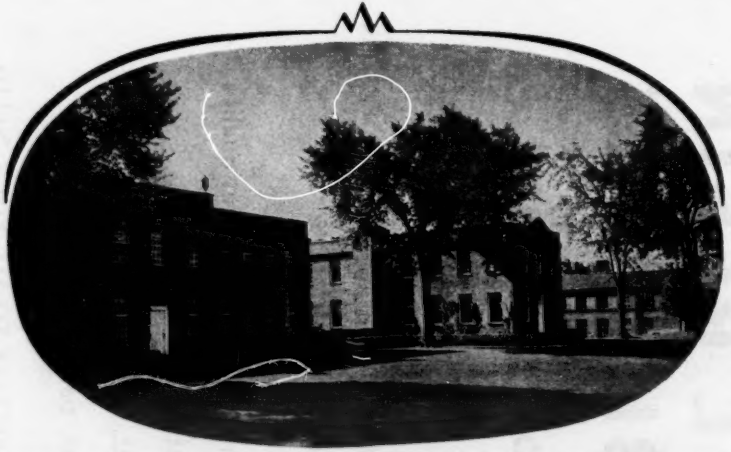
INDEX TO ADVERTISERS

	PAGE
Advance Solvents & Chemical Corp. (Opposite Inside Back Cover)	38
American Cyanamid Company, Calco Chemical Division	13
American Zinc Sales Company	22
Barrett Div., The, Allied Chemical & Dye Corp.	21
Binney & Smith Company (Opposite Table of Contents)	16
Bolling, Stewart & Company, Inc.	6
Cabot, Godfrey L., Inc.	11
Carter Bell Manufacturing Company, The	28
Du Pont Grasselli Chemicals Department	31
Du Pont Rubber Chemicals Division	30
Flintkote Company, The	4
General Atlas Carbon Company	33
Goodrich, B. F., Chemical Company (Hycar)	8
Goodyear Tire & Rubber Company, The	5
Gall, C. P. Company, The	23
Harwick Standard Chemical Company	20
Huber, J. M., Corporation	18
India Rubber World	27
Monsanto Chemical Company	12
Muehlstein, H. & Company, Inc.	9
Naugatuck Chemical Division (U. S. Rubber Company)	17
Neville Company, The	32
New Jersey Zinc Company, The	Outside Back Cover
Pennsylvania Industrial Chemical Corporation	35
Pequanoc Rubber Company	Inside Back Cover
Phillips Chemical Company	2
Pittsburgh Plate Glass Company, Columbia Chemical Div.	28
Rare Metal Products Company	34
Richardson, Sid Carbon Company	7
Rubber Age, The	25
St. Joseph Lead Company	24
Scott Testers, Inc.	26
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	29
Stamford Rubber Supply Company, The	23
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	14
Thiokol Corporation, The	10
Titanium Pigment Corporation	18
Union Bay State Chemical Company	19
United Carbon Company	Inside Front Cover
Vanderbilt R. T. Company	37
Witco Chemical Company	Opposite Inside Front Cover 1



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AMONG WHITE PIGMENTS

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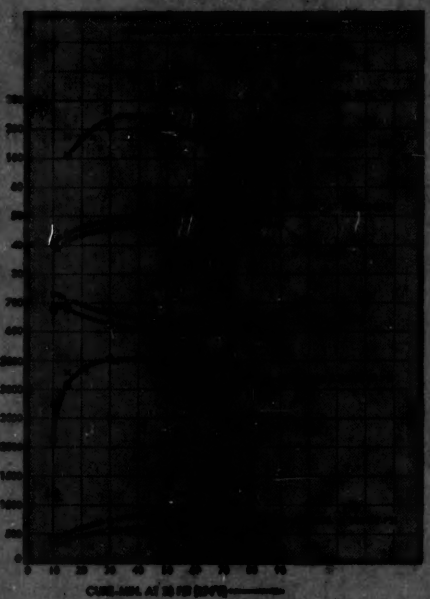

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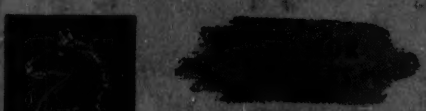
Albalith-73 is a special, surface-treated lithopone, processed to give better dispersion and fewer aggregates in rubber. Its greater surface area in contact with rubber produces higher tensiles and tear resistance.

Albalith-73 compares favorably with Protox-166 Zinc Oxide*, for example, in tensiles and tear resistance — although it of course does not activate accelerators. See accompanying stress-strain chart.

Compare **Albalith-73** with Zinc Oxide and other white pigments for reinforcement in your compounds now.

COMPOUND	
Smoked Sheet	100
Sulfur	3
MBT	1
Agerite Powder	1
Stearic Acid	3
Protox-166	100- S
Lithopone	0-90.0

*U.S. Patents 2,590,229 and 2,590,230